# Molecular Inhomogeneity and Amplitude of Scattering of the Products of Diblock Copolymer Degradation

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ABSTRACT: Expressions are derived for the distributions in size and composition of the macromolecular products of random degradation of diblock copolymers with arbitrary block length distributions. Equations for the calculation of the angular dependence of the static structure factor of these products formed at different depths of degradation are presented. General regularities of the evolution of the spinodal of the polymer melt in the course of this reaction are analyzed. Proceeding from the general theory developed, examples concerning degradation processes of diblock copolymers with particular block length distributions are provided.

## I. Introduction

The investigation of the degradation processes of polymers is of utmost significance for macromolecular chemistry.[1,2] The chemical transformation of polymers induced by their fragmentation usually leads to an unwanted deterioration of the service properties of polymeric materials. The change of some important statistical characteristics of a polymer sample (e.g., its molecular weight distribution, MWD, describing the molecular inhomogeneity of homopolymers) due to the degradation of polymer chains is obviously responsible for this deterioration. On the other hand, for some applications, such as biomedical, degradation may even be often a desirable property.[3,4] However, also in that case knowledge of the evolution of the performance properties is essential. In the case of binary copolymers, the macromolecules differ in numbers $l_1$ and $l_2$ of monomeric units $M_1$ and $M_2$ which unambiguously characterize their size $l = l_1 + l_2$ and chemical composition $\zeta_1 = l_1/l$, $\zeta_2 = l_2/l$. The joint distribution of molecules for size and composition (SCD) describes the molecular inhomogeneity. To the authors' knowledge, no attempts to consider theoretically the evolution of such a SCD in the course of the process of diblock copolymer degradation have been undertaken so far. For homopolymer analogues, though more simple, the problem of the alteration of the MWD of the products of degradation was tackled.[5−7]

A specific feature of diblock copolymers is the possibility of phase separation during degradation. This phenomenon results from an appreciable increase in composition inhomogeneity due to the contribution of homopolymers, whose fractions progressively increase with the growth of the degradation depth. When this factor prevails over the decrease of the average size of the macromolecules, which favors the stability of the homogeneous state, the system may exhibit phase separation. The capacity to predict such a destruction-induced phase transition, which may lead to a loss of transparency of the polymer system and a deterioration of some of its performance properties, is of indisputable practical interest because polymeric materials are known to undergo degradation during their processing and aging. The opposite situation is also quite conceivable when in the course of degradation the interplay of the above two factors will cause the annihilation of spatially periodic structures formed in melts of diblock copolymers. Revealing the conditions of such annihilation by means of mathematical modeling constitutes a challenging task when predicting the properties of advanced polymer materials based on block copolymers.

The most straightforward way to measure the thermodynamic miscibility of polymer liquids is via scattering techniques, namely, light, X-ray, or neutron scattering.[8,9] Measuring the angular dependence of the static structure factor provides valuable information on the thermodynamic state of a polymer liquid. The calculation of this dependence within the framework of the random phase approximation (RPA) was reported for block copolymers of different architecture.[10−13] However, with respect to the products of their degradation such a calculation has not been done so far. Its inherent peculiarity consists of the fact that to have this problem solved, it is necessary to first find the dependence on time of the SCD of macromolecules being formed during the degradation process of the initial block copolymer system.

The solution of this problem of statistical chemistry of polymers will be discussed in the next section of this paper. In the third section the equations will be derived which describe within the framework of RPA the evolution of the structure factor of the products of degradation of diblock copolymers with an arbitrary distribution of block lengths. Furthermore, equations describing the spinodal and the Lifshitz points in the melt of such copolymers will be presented. The last section will be devoted to the illustration of the applicability of the general theory developed to the degradation of diblock copolymers whose block length distributions are either monodisperse or exponential.

## II. Statistical Chemistry of Degraded Diblock Copolymers

The theoretical investigation of diblock copolymer degradation requires as a first step to write down a

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kinetic scheme for the chemical transformations of the macromolecules. Below we will consider random chain scission rather than a depolymerization mechanism of degradation,[1] assuming that the Flory principle works. This means that any intramolecular bond entering into the α-th type block (α = 1, 2) is broken within an infinitely small interval of time d$t$ with infinitesimal probability $k_\alpha$d$t$. Consequently, the model comprises only two kinetic parameters, $k_1$ and $k_2$, being the chemical bond cleavage rate constants of bonds of the first and the second type, respectively. This simplest model of degradation, based on the applicability of the fundamental Flory principle, is most widespread in polymer chemistry. However, violation of this principle can occur in some systems due to, for instance, shear acting on macromolecules.

If a diblock copolymer molecule, whose block lengths are $l_1$ and $l_2$, is designated as $\{l_1, l_2\}$, the kinetic scheme of the molecular reactions will be

$$\{l_1, l_2\} \xrightarrow{k_1 l_1} \{l_1', l_2\} + \{l_1'', 0\}, \quad l_1' + l_1'' = l_1, \quad l_2 \geq 0$$

$$\{l_1, l_2\} \xrightarrow{k_2 l_2} \{l_1, l_2'\} + \{0, l_2''\}, \quad l_2' + l_2'' = l_2, \quad l_1 \geq 0 \quad (1)$$

Let $C_1$ ($l_1$), $C_2$ ($l_2$), and $C_{12}$ ($l_1$, $l_2$) denote the dimensionless concentrations of the homopolymers $\{l_1, 0\}$ and $\{0, l_2\}$ and diblock copolymer $\{l_1, l_2\}$ (reduced to the overall concentration of monomeric units) which are present in the reaction system at time $t$. The kinetic equations for these concentrations corresponding to scheme (eq 1) read

$$\frac{dC_{12}(l_1,l_2)}{dt} = k_1\int_{l_1}^{\infty} C_{12}(\xi_1,l_2)\, d\xi_1 + k_2\int_{l_2}^{\infty} C_{12}(l_1,\xi_2)\, d\xi_2 - (k_1 l_1 + k_2 l_2)C_{12}(l_1,l_2) \quad (2)$$

$$\frac{dC_1(l_1)}{dt} = k_1\int_0^{\infty} dl_2 \int_{l_1}^{\infty} C_{12}(\xi_1,l_2)\, d\xi_1 + 2k_1\int_{l_1}^{\infty} C_1(\xi_1)\, d\xi_1 - k_1 l_1 C_1(l_1) \quad (3)$$

$$\frac{dC_2(l_2)}{dt} = k_2\int_0^{\infty} dl_1 \int_{l_2}^{\infty} C_{12}(l_1, \xi_2)\, d\xi_2 + 2k_2 \int_{l_2}^{\infty} C_2(\xi_2)\, d\xi_2 - k_2 l_2 C_2(l_2) \quad (4)$$

These equations will be solved below under the following initial conditions

$$C_{12}^0(l_1,l_2) = Y^0 f_1^0(l_1)\, f_2^0(l_2), \quad C_1^0(l_1)\, C_2^0(l_2) = 0 \quad (5)$$

where $f_\alpha^0(l_\alpha)$ represents the MWD of the α-th type blocks (α = 1, 2) in the initial copolymer while $Y^0 = \Pi^0/M$ stands for the ratio of the concentrations of all its molecules $\Pi^0$ to the concentration $M$ of monomeric units involved in them. Evidently, $Y^0$ is nothing but the reciprocal number-average degree of polymerization $\bar{l}^0$ of the initial copolymer system. As for the function $C_{12}^0(l_1,l_2)$, its assumed factorization (eq 5) suggests the independence of the length distributions of the different types of blocks. This condition is likely to hold for most ways of diblock copolymer synthesis. In the case of the presence of some fraction of homopolymers (typical for commercial block copolymers) in a specimen undergoing degradation, the initial condition (eq 5) admits the extension allowing for this circumstance.

The solution of the Cauchy problem (eqs 2−5), given in the Appendix, may be presented as follows

$$C_{12}(l_1,l_2) = C_{12} f_1(l_1)\, f_2(l_2), \quad \text{where } C_{12} = C_{12}^0 = Y^0 \quad (6)$$

$$C_\alpha(l_\alpha) = C_\alpha f_\alpha^h(l_\alpha)\ (\alpha = 1, 2), \quad \text{where } C_\alpha = k_\alpha X_\alpha \bar{l}^0 t = Z_\alpha \tau \quad (7)$$

Here $f_1(l_1)$ and $f_2(l_2)$ denote the MWD of blocks of monomeric units $M_1$ and $M_2$ at time $t$

$$f_\alpha(l_\alpha) = \exp(-\tau_\alpha l_\alpha)[f_\alpha^0(l_\alpha) + \tau_\alpha\int_{l_\alpha}^{\infty} f_\alpha^0(\xi)\, d\xi] \quad (\alpha = 1, 2) \quad (8)$$

whereas $f_1^h(l_1)$ and $f_2^h(l_2)$ are the MWDs of the first and second type homopolymers

$$f_\alpha^h(l_\alpha) = \frac{\exp(-\tau_\alpha l_\alpha)}{\bar{l}_\alpha^0}\int_{l_\alpha}^{\infty}[1 + \tau_\alpha(\xi - l_\alpha)] f_\alpha^0(\xi)\, d\xi \quad (\alpha = 1, 2) \quad (9)$$

In expressions 6−9 use is made of the following designations

$$\tau_\alpha = k_\alpha t, \quad \tau = (k_1\bar{l}_1^0 + k_2\bar{l}_2^0)t, \quad \bar{l}_\alpha^0 = X_\alpha \bar{l}^0, \quad Z_\alpha = \frac{k_\alpha X_\alpha}{k_1 X_1 + k_2 X_2} \quad (10)$$

Here $\bar{l}_\alpha^0$ stands for the number-average length of the α-th type block in the initial block copolymer, where the molar fractions of units $M_1$ and $M_2$ are $X_1$ and $X_2$. These quantities, $X_\alpha$, representing number-average values of the degradation products' composition, remain unchanged in the course of degradation. The same property is also inherent to the overall concentration $C_{12}$ (eq 6) of block copolymer molecules.

It is possible to separate homopolymers formed as a result of the degradation process from block copolymers by means of a chromatographic technique. Consequently, by plotting the experimental dependencies on time of the concentration of the two homopolymers formed during the degradation of the initial block copolymer, one can find the values of both kinetic parameters, $k_1$ and $k_2$, characterizing the model at hand.

A comparison of the MWDs of these homopolymers calculated by eq 9 with the experimental MWDs allows a verification of the adequacy of the degradation model chosen. Such a comparison is easier to realize with respect to the statistical moments of the MWD than with respect to the very distribution itself. Explicit formulas for them can be derived (see Appendix) provided analytical expressions are known for the generating functions $g_\alpha^0(p)$ of the MWD $f_\alpha^0(l_\alpha)$ of blocks in the initial diblock copolymer. The simplest criterion for the applicability of the model of random degradation is the proportionality of the overall concentration of homopolymer molecules, $C_\alpha$, to the degradation time $t$. Proceeding from eq 7, it is easy to determine the constant of degradation $k_\alpha$ from the slope of the straight line of $C_\alpha$ versus $t$. Recourse to the cross-fractionation method[14,15] provides the possibility to separate block copolymer macromolecules by their size $l = l_1 + l_2$, irrespective of composition. The equation allowing to find the distribu-

tion $f^{s}_{12}(l)$ of the block copolymer molecules for $l$ can be derived analytically (see Appendix).

### III. Statistical Physics of Degraded Diblock Copolymers

To calculate within the framework of the RPA, the scattering intensity $I(q)$ of a melt of an arbitrary incompressible mixture of macromolecules with two blocks of different types of monomeric units $M_1$ and $M_2$, it is possible to resort to well-known relations[10−13]

$$I(q) = \frac{M(a_1 - a_2)^2}{D(q)}, \quad D(q) = H(q) - 2\chi \tag{11}$$

$$H(q) = \frac{\tilde{X}_{11} + \tilde{X}_{22} + 2\tilde{X}_{12}}{\tilde{X}_{11}\tilde{X}_{22} - \tilde{X}_{12}^2} \tag{12}$$

where $q$ represents the modulus of the scattering wave vector, $a_1$ and $a_2$ are the scattering lengths of units $M_1$ and $M_2$, and $\chi$ is the Flory−Huggins interaction parameter. As for the elements $\tilde{\kappa}_{\alpha\beta} = M\tilde{X}_{\alpha\beta}$ of the structure matrix, their dependence on $q$ is defined by the expressions

$$\tilde{X}_{\alpha\alpha}(q) = 2\int_0^\infty C_\alpha^b \, \mathrm{d}l_\alpha \int_0^{l_\alpha} \mathrm{d}\eta \int_0^\eta \mathrm{d}\xi \, \exp[-Q\xi] \quad (\alpha = 1, 2) \tag{13}$$

$$\bar{X}_{12}(q) = \int_0^\infty \int_0^\infty C_{12}(l_1, l_2) \, \mathrm{d}l_1 \, \mathrm{d}l_2 \int_0^{l_1} \mathrm{d}\eta_1 \int_{l_1}^{l_1+l_2} \mathrm{d}\eta_2 \, [-Q(\eta_2 - \eta_1)] \tag{14}$$

where the following designations are employed

$$Q = \frac{a^2 q^2}{6} \qquad C_\alpha^b(l_\alpha) = C_\alpha(l_\alpha) + Y^0 f_\alpha(l_\alpha) \tag{15}$$

for the dimensionless square of the wave vector $q$ with monomeric unit size $a$ as a scale and dimensionless concentration $C_\alpha^b(l_\alpha)$ of the α-th type blocks with $l_\alpha$ monomeric units. Knowing the Laplace transform of this function, $\tilde{C}_\alpha^b(p)$, it is easy to find the diagonal elements of the structure matrix

$$\tilde{X}_{\alpha\alpha}(Q) = \frac{2}{Q^2}[\tilde{C}_\alpha^b(Q) - \tilde{C}_\alpha^b(0) + X_\alpha Q] \quad (\alpha = 1, 2) \tag{16}$$

In conformity with eq 15, $\tilde{C}_\alpha^b(p)$ represents a linear combination of generating functions $g_\alpha(p)$ and $g_\alpha^h(p)$ of distributions $f_\alpha(l_\alpha)$ (eq 8) and $f_\alpha^h(l_\alpha)$ (eq 9), the expressions for which are derived in the Appendix. Making use of expressions A8 and A9 as well as of the relations 15 and 16, we get the final expression for the matrix elements $\tilde{X}_{11}(Q)$ and $\tilde{X}_{22}(Q)$

$$\tilde{X}_{\alpha\alpha}(Q) = \frac{2Y^0}{(\hat{Q}_\alpha)^2}[g_\alpha^0(\hat{Q}_\alpha) - 1 + \tilde{l}_\alpha^0 \hat{Q}_\alpha], \quad \hat{Q}_\alpha = Q + \tau_\alpha \tag{17}$$

Just in the same way by means of the expressions 14, 6, and A8, the equation for the nondiagonal elements of the structure matrix

$$\tilde{X}_{12}(Q) = \tilde{X}_{21}(Q) = \frac{Y^0}{\hat{Q}_1 \hat{Q}_2}[1 - g_1^0(\hat{Q}_1)][1 - g_2^0(\hat{Q}_2)] \tag{18}$$

can be derived. To switch to natural scales of the values of the variables, it is convenient to use variables $l_\alpha/\bar{l}_\alpha^0$ rather than $l_\alpha$. In terms of these rescaled variables, eqs 17 and 18 assume the form

$$\tilde{X}_{\alpha\alpha}(y) = \frac{2\tilde{l}^0 X_\alpha^2}{(\hat{y}_\alpha)^2}[\hat{g}_\alpha^0(\hat{y}_\alpha) - 1 + \hat{y}_\alpha] \quad (\alpha = 1, 2) \tag{19}$$

$$\tilde{X}_{12}(y) = \tilde{X}_{21}(y) = \frac{\bar{l}^0 X_1 X_2}{\hat{y}_1 \hat{y}_2}[1 - \hat{g}_1^0(y_1)][1 - \hat{g}_2^0(\hat{y}_2)] \tag{20}$$

Here additional designations are introduced

$$\hat{y}_\alpha = \bar{l}_\alpha^0 \hat{Q}_\alpha = X_\alpha y + Z_\alpha \tau, \quad y = Q\tilde{l}^0 = q^2\overline{R_G^2}, \quad \overline{R_G^2} = \frac{a^2 \bar{l}^0}{6} \tag{21}$$

where the dimensionless time $\tau$ and the parameter $Z_\alpha$ have, consequently, the meaning of the average number of cleavages per macromolecule and the fraction of these cleavages occurring in α-th type blocks. In expressions 19 and 20 $\hat{g}_\alpha^0(p)$ stands for the generating function of the stochastic variable $l_\alpha/\bar{l}_\alpha^0$ distribution in molecules of the initial block copolymer. Substituting expressions 19 and 20 for the elements of the structure matrix into eq 12 enables one to find the expression for the scattering intensity (eq 11) of the products of a diblock copolymer degradation at arbitrary depth of this reaction. Examples of the employment of this expression, derived for arbitrary MWDs of blocks for lengths, will be provided in the next section where we specialize to systems with specified MWDs.

An important element of a phase diagram is the spinodal, i.e., a hypersurface within the space of external parameters of a system where the latter loses local stability of the spatially homogeneous state. The mathematical condition of the spinodal, where the amplitude of scattering (eq 11), becomes infinite is as follows

$$H_m = 2\chi, \quad \text{where } H_m \equiv \min_q H(q) = H(q^*) \tag{22}$$

The function $H(q)$ (eq 12) can reach its minimum value $H_m$ either at zero wave vector, $q^* = 0$, or at $q^* \neq 0$. In the first case we deal with the trivial branch of the spinodal, whereas in the second case we deal with its nontrivial branch. Equations for these hypersurfaces within the parametric space read respectively

$$1)\ 2\chi = H(0) \quad 2)\ 2\chi = H(q^*), \quad H'(q^*) = 0, \quad H''(q^*) > 0 \tag{23}$$

where $H'(q)$ and $H''(q)$ denote the first- and second-order derivatives of the function $H(q)$. The trivial and nontrivial branches of the spinodal are separated by the Lifshitz point hyperline which can be found using the equations

$$2\chi = H(0), \quad H''(0) = 0, \quad H''''(0) > 0 \tag{24}$$

For the system under consideration, the function $H$ (eq 12) depends on $q$ only through the variable $y = q^2\overline{R_G^2}$ so that for theoretical considerations it is convenient to use the function $\mathcal{H}(y) \equiv H(q^2\overline{R_G^2}) = H(q)$ instead of $H(q)$. The derivatives of these functions are connected by

simple relations

$$H'(q) = 2q\overline{R_G^2}H\ '(y),$$
$$H''(q) = 2\overline{R_G^2}[2yH\ ''(y) + H\ '(y)] \quad (25)$$

which allows to rewrite eq 23 for the spinodal in terms of the function $H(y)$

$$1)\ 2\chi = H(0) \quad 2)\ 2\chi = H(y^*), \quad H\ '(y^*) = 0, \quad H\ ''(y^*) > 0 \quad (26)$$

and eq 24 for the Lifshitz point

$$2\chi = H(0), \quad H\ '(0) = 0, \quad H\ ''(0) > 0 \quad (27)$$

The function $H$ depending on the variable $y = q^2\overline{R_G^2}$ (eq 21) and the dimensionless time $\tau$ (eq 10) is also controlled by a set of external parameters both chemical and physical in nature. To the chemical parameters, the reactivity ratio $r = k_1/k_2$ belongs, characterizing the difference in stability of the chemical bonds involved in blocks of different type. More appropiate for numerical calculations is the kinetic parameter $U_1 = 1 - U_2 = k_1/(k_1 + k_2)$, since its value lies within the interval [0,1]. To the physical parameters, the set pertains comprising the composition of the initial block copolymer **X** and the parameters of the MWD of its blocks.

The theory developed above allows us to answer at least two questions of practical interest. The first question, which is relevant to the thermodynamics of reacting "living" systems, is whether the loss of thermodynamic stability of the initial homogeneous state will happen in the course of the degradation process. And, if so, will it occur at zero or nonzero wave vector $q^*$? The second question is what the spinodal will be of the "dead" system comprising the products of the degradation of the initial block copolymer formed during a specified time of degradation. This system being cooled with a rate perceptible exceeding that of degradation will reach the spinodal at a certain temperature $T_s$. The answer to the second question for a known dependence of the parameter $\chi$ on temperature enables us to reveal a region of those values of external parameters inside which the polymer specimen can be cooled to a fixed temperature $T$ with no loss in local stability of its spatially homogeneous state. Otherwise stated, it enables us to find the area of the parametric space where $T_s < T$.

It is natural to start the examination of the evolution of the spinodal in the course of degradation with the analysis of its appearance in the melt of the initial block copolymer. To this end expressions may be used for the function $H(y)$ and its derivative $H\ '$ at point $y = 0$

$$H(0) = \frac{K_1X_1^2 + K_2X_2^2 + 2X_1X_2}{\bar{l}^0(X_1X_2)^2(K_1K_2 - 1)}, \quad H\ '(0) = \frac{\Delta(\mathbf{X})}{3(X_1X_2)^2(K_1K_2 - 1)^2} \quad (28)$$

$$\Delta(\mathbf{X}) = K_1'K_1^2X_1(X_1 + K_2X_2)^2 + K_2'K_2^2X_2(K_1X_1 + X_2)^2 - 3(K_1X_1 + K_2X_2)(X_1 + K_2X_2)(K_1X_1 + X_2) \quad (29)$$

The coefficients of the cubic polynomial (eq 29) are controlled exclusively by polydispersity coefficients $K_\alpha$ and $K_\alpha'$ of the MWD of α-th type blocks (α = 1, 2) in the initial copolymer which are related to number-average, $P_{n\alpha}$, weight-average, $P_{w\alpha}$, and $z$-average, $P_{z\alpha}$, degrees of polymerization of these blocks by simple relationships

$$K_\alpha \equiv \frac{P_{w\alpha}}{P_{n\alpha}} = \frac{\overline{l_\alpha^2}}{\bar{l}_\alpha\bar{l}_\alpha} \qquad K_\alpha' \equiv \frac{P_{z\alpha}}{P_{w\alpha}} = \frac{\overline{l_\alpha^3}\bar{l}_\alpha}{\overline{l_\alpha^2}\,\overline{l_\alpha^2}} \quad (30)$$

Here for simplicity superscript "0" is omitted from the designation of the $n$-order statistical moments $\overline{l_\alpha^n}$ of the MWD $f_\alpha^0(l_\alpha)$.

The sign of the quantity Δ is of central importance for the spinodal analysis. Thus, for instance, in the case of monodisperse block copolymers the spinodal is known[16] to have no trivial branch at all. Will polydisperse copolymer contain such a branch? A necessary condition for this is the positiveness of Δ. If the function $H(y)$ has no more than one minimum, then the implementation of the inequality Δ > 0 is not only a necessary but also a sufficient condition for a spatially homogeneous state of a system to lose its stability just at zero wave vector value during cooling. For systems exhibiting such a typical behavior of the function $H(y)$, zeroes of the polynomial Δ($x$) (eq 29) inside the unit interval (0, 1) correspond to the Lifshitz points dividing this unit segment into intervals within each of which the quantity Δ does not change its sign. Those intervals where it is positive or negative correspond to trivial or nontrivial spinodal branches, respectively. To find them recourse should be made to eqs 26, 28, and 29 while it is possible to calculate the Lifshitz points using eq 27.

All initial diblock copolymers (proceeding from the shape of their spinodal $\chi = F_S(\mathbf{X})$) can be subdivided into four types according to the number of roots $i$ = 0, 1, 2, 3 of polynomial Δ($x$) (eq 29) inside the unit interval. This number may be even or odd depending on whether the quantity $\delta = (K_1' - 3)(K_2' - 3)$ is positive or negative. Consequently, the condition $\delta < 0$ is sufficient for the existence of at least one Lifshitz point and, thus, for the existence of a trivial branch of the spinodal $\chi = F_S(\mathbf{X})$.

To reveal how many roots polynomial Δ($x$) (eq 29) has inside the unit segment it is necessary to calculate the sign of the expression

$$D = B^2C^2 - 4AC^3 - 4B^3D - 27A^2D^2 + 18ABCD \quad (31)$$

where the following designations are employed

$$A = (K_1' - 3)K_1^2, \quad B = K_1[2K_1'K_1K_2 + K_2'K_1K_2^2 - 3(K_1K_2 + K_2 + 1)]$$
$$C = K_2[K_1'K_1^2K_2 + 2K_2'K_1K_2 - 3(K_1K_2 + K_1 + 1)], \quad D = (K_2' - 3)K_2^2 \quad (32)$$

If $D < 0$, then polynomial Δ(**X**) has only one root having a physical meaning. Conversely, when $D > 0$, the number of such roots coincides with the number of sign reversals in the sequence $A,B,C,D$ defined in (eq 32). Hence, the question of classification of conceivable spinodal forms may be considered as settled.

Concluding this section, it is pertinent to point out unambiguously the correlation between the shape of curves $H(q)$ and $I(q)$. So, every minimum of the first one corresponds to a maximum of the second one. This

means that when measuring the angular dependence of the amplitude of scattering, it is possible to predict at which particular spinodal branch, trivial or nontrivial, the system will loose the stability of the spatially homogeneous state under cooling. Essentially, it is possible to carry out the scattering experiments at a temperature which is higher than that corresponding to the cloud point curve. The advantages of performing these experiments in the region of absolute thermodynamic stability of the homogeneous state instead of in the metastable region are beyond any doubt.

## IV. Applications

The distribution of the blocks for lengths in an initial copolymer is evidently predetermined by the conditions of its synthesis. If the block formation follows the mechanism of "living" anionic polymerization, their distribution is close to monodisperse, i.e., it is described by the Dirac delta-function

$$f_\alpha^0(l_\alpha) = \delta(N_\alpha - l_\alpha), \quad g_\alpha^0(y_\alpha) = \exp(-N_\alpha y_\alpha), \quad \hat{g}_\alpha^0(y_\alpha) = \exp(-y_\alpha) \tag{33}$$

where $N_\alpha$ is the number of units involved in an α-th type block. When blocks are prepared by the methods of free-radical polymerization or polycondensation, their distribution is often a nearly exponential one

$$f_\alpha^0(l_\alpha) = \epsilon_\alpha \exp(-\epsilon_\alpha l_\alpha), \quad g_\alpha^0(y_\alpha) = \frac{1}{1 + \bar{l}_\alpha^0 y_\alpha}, \quad \hat{g}_\alpha^0(y_\alpha) = \frac{1}{1 + y_\alpha} \tag{34}$$

where $\epsilon_\alpha = 1/\bar{l}_\alpha^0$ is the reciprocal average number of units in an α-th type block. Polydispersity coefficients (eq 30) of the monodisperse (eq 33) and the Flory distribution (eq 34) are respectively

$$1)\ K_\alpha = K'_\alpha = 1 \qquad 2)\ K_\alpha = 2, \quad K'_\alpha = \frac{3}{2} \tag{35}$$

Proceeding from eqs 8 or A8, it is possible to derive the expressions

$$f_\alpha(l_\alpha) = \exp(-\tau_\alpha l_\alpha)[\delta(N_\alpha - l_\alpha) + \tau_\alpha \eta_s(N_\alpha - l_\alpha)] \tag{36}$$

$$f_\alpha(l_\alpha) = \hat{\epsilon}_\alpha \exp(-\hat{\epsilon}_\alpha l_\alpha), \quad \text{where } \hat{\epsilon}_\alpha = \epsilon_\alpha + \tau_\alpha \tag{37}$$

characterizing respectively the evolution of initial distributions (eqs 33 and 34) of the α-th type blocks for lengths $l_\alpha$ in the course of the degradation. Henceforward, $\eta_s$ stands for the Heaviside step function. The MWD of homopolymers formed during the degradation process of monodisperse and exponentially distributed blocks are described by the following formulas

$$f_\alpha^h(l_\alpha) = \frac{\exp(-\tau_\alpha l_\alpha)}{N_\alpha}[1 + \tau_\alpha(N_\alpha - l_\alpha)]\eta_s(N_\alpha - l_\alpha) \tag{38}$$

$$f_\alpha^h(l_\alpha) = \hat{\epsilon}_\alpha \exp(-\hat{\epsilon}_\alpha l_\alpha) \tag{39}$$

which may be readily derived using expression 9 or A9 with allowance for eqs 33 and 34, respectively. Noteworthy, the distribution eqs 37 and 39, unlike eqs 36 and 38, coincide with one another and with the initial distribution (eq 34) upon the replacement in the latter of the parameter $\epsilon_\alpha$ by $\hat{\epsilon}_\alpha$. General formulas A10 and A11 in the case of monodisperse blocks yield the following expressions for the statistical characteristics of the degradation products

$$\bar{l}_\alpha = \frac{N_\alpha}{\theta_\alpha}(1 - e^{-\theta_\alpha}), \quad \sigma_\alpha^2 = \frac{N_\alpha^2}{\theta_\alpha^2}(1 - 2\theta_\alpha e^{-\theta}\alpha - e^{-2\theta_\alpha}), \quad \text{where } \theta_\alpha = N_\alpha \tau_\alpha \tag{40}$$

$$P_{n\alpha}^h = \frac{N_\alpha}{\theta_\alpha^2}(\theta_\alpha - 1 + e^{-\theta_\alpha}), \quad K_\alpha^h = \frac{2\theta_\alpha[\theta_\alpha(1 + e^{-\theta_\alpha}) - 2(1 - e^{-\theta_\alpha})]}{(\theta_\alpha - 1 + e^{-\theta_\alpha})^2} \tag{41}$$

Analogous formulas for exponentially distributed blocks read

$$\bar{l}_\alpha = P_{n\alpha}^h = \hat{\epsilon}_\alpha^{-1}, \quad \sigma_\alpha^2 = \hat{\epsilon}_\alpha^{-2}, \quad K_\alpha^h = 2 \tag{42}$$

Below we will consider three types of initial diblock copolymers

$$I)\ MD + MD \qquad II)\ MD + F \qquad III)\ F + F \tag{43}$$

composed of monodisperse blocks (MD) and those characterized by the Flory exponential distribution (F). The SCD of the products of degradation of these copolymers is described by the expression

$$f_{12}(l,\zeta) = l f_1(l\zeta_1)\, f_2(l\zeta_2) \tag{44}$$

where the pair of functions $f_1(l_1)$ and $f_2(l_2)$ are picked out of (eq 36, eq 37), depending on the type of initial copolymers (eq 43). So, for instance, to get an idea of the evolution of the distribution (eq 44) for type III, it is possible to turn to Figure 1. An interesting peculiarity of this evolution is the fact that under the condition $(X_2 - X_1)(U_2 - U_1) > 0$ a unique instant of time does exist, $\tau^* = (X_2 - X_1)(U_1X_1 + U_2X_2)/X_1X_2(U_2 - U_1)$, when the SCD (eq 44) does not depend on composition ζ (Figure 1.2), therefore degenerating into a one-dimensional distribution

$$f_{12}(l,\zeta) = \hat{\epsilon}^2 l \exp(-\hat{\epsilon}_l), \quad \text{where } \hat{\epsilon} = \hat{\epsilon}_1 = \hat{\epsilon}_2 = \frac{U_2X_2 - U_1X_1}{\bar{l}^0(U_2 - U_1)X_1X_2} \tag{45}$$

Substituting into formula A8 expressions 33 and 34 for $g_\alpha^0$ results in the Laplace transforms of the distributions for the block length $l_\alpha$ in degraded copolymer molecules. Further, making use of formula A12, it is possible to derive expressions for the distribution of these molecules $f_{12}^s$ for their size $l$ for the three types (eq 43) of initial copolymers

$$I)\quad f_{12}^s(l) = \exp(-\tau_1 N_1 - \tau_2 N_2)\,\delta(l - N) + \frac{\tau_1 \exp(-\tau_1 l)}{\tau_2 - \tau_1}\{\tau_2 \eta_s(N_1 - l) - \tau_1 \exp[(\tau_1 - \tau_2)N_2][\eta_s(l - N_2) - \eta_s(l - N)]\} + \frac{\tau_2 \exp(-\tau_2 l)}{\tau_1 - \tau_2}\{\tau_1 \eta_s(N_2 - l) - \tau_2 \exp[(\tau_2 - \tau_1)N_1][\eta_s(l - N_1) - \eta_s(l - N)]\} \tag{46}$$

$$II)\ f^{s}_{12}(l) = \frac{\hat{\epsilon}_2}{\hat{\epsilon}_2 - \tau_1}\{\tau_1 \exp(-\tau_1 l)\,\eta_s(N_1 - l) + \exp(-\hat{\epsilon}_2 l)[\hat{\epsilon}_2 \exp[(\hat{\epsilon}_2 - \tau_1)N_1]\eta_s(l - N_1) - \tau_1]\} \quad (47)$$

$$III)\ f^{s}_{12}(l) = \frac{\hat{\epsilon}_1\hat{\epsilon}_2}{\hat{\epsilon}_2 - \hat{\epsilon}_1}[\exp(-\hat{\epsilon}_1 l) - \exp(-\hat{\epsilon}_2 l)] \quad (48)$$

The random variable $l = l_1 + l_2$, being the sum of two independent random variables $l_1$ and $l_2$, has the center $\bar{l}_2 + \bar{l}_2$ and the dispersion $\sigma_1^2 + \sigma_2^2$, where $\bar{l}_\alpha$ and $\sigma_\alpha^2$ were determined above for monodisperse (eq 40) and exponentially distributed (eq 42) blocks.

The integration of expression 44 over the variable $l$ results in the one-dimensional distribution $f^{c}_{12}(\zeta)$ of the degradation products which for the initial diblock copolymer of type III takes the form

$$f^{c}_{12}(\zeta) = \frac{\hat{\epsilon}_1\hat{\epsilon}_2}{(\hat{\epsilon}_1\zeta_1 + \hat{\epsilon}_2\zeta_2)^2} \quad (49)$$

Owing to its monotonicity, this function reaches its maximum value at one of the edges of the unit segment $\zeta_1 + \zeta_2 = 1$. This edge corresponds to the α-th homopolymer for which the value of the parameter $\hat{\epsilon}_\alpha$ is least. The composition distribution (eq 49) is controlled by only one parameter which is the ratio between the quantities $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$. The more they differ, the narrower this distribution is. The largest composition inhomogeneity occurs for $\hat{\epsilon}_1 = \hat{\epsilon}_2$, when any value of block copolymer composition turns out to be equiprobable. In order for this case to be realized during the degradation process, it is necessary and sufficient for the initial copolymer to contain in excess those units whose blocks are more prone to the cleavage. The mathematical condition for this is the inequality $(X_2 - X_1)(k_2 - k_1) > 0$. If this condition is met, then the block copolymer composition inhomogeneity first rises in the beginning of the degradation up to the moment $\tau^* = (X_2 - X_1)(U_1X_1 + U_2X_2)/X_1X_2(U_2 - U_1)$, when the quantities $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ become equal to one another, and then starts to decrease. Conversely, if the inequality $(X_2 - X_1)(k_2 - k_1) < 0$ holds, then the composition distribution (eq 49) gets monotonically narrower during the whole degradation process.

As for the distribution (eq 48) of the size of the degradation products of macromolecules of type III, the evolution of its width in case $(X_2 - X_1)(k_2 - k_1) > 0$ proceeds in opposite direction as compared to the alteration of the width of the composition distribution (eq 49). This conclusion ensues from the analysis of the expression

$$K = 2[1 - (\sqrt{\hat{\epsilon}_1/\hat{\epsilon}_2} + \sqrt{\hat{\epsilon}_2/\hat{\epsilon}_1})^{-2}] \quad (50)$$

for the polydispersity coefficient of distribution (eq 48). It decreases from the value $K^0 = 1 + X_1^2 + X_2^2$ at $\tau = 0$ up to the value $K^* = {}^3/_2$ at $\tau = \tau^*$ and then rises tending to the quantity $K^\infty = 1 + U_1^2 + U_2^2$. Conversely, in case $(X_2 - X_1)(k_2 - k_1) < 0$ the coefficient (eq 50) changes monotonically from $K^0$ to $K^\infty$. Examples demonstrating the above-mentioned regularities of the evolution of one-dimensional distributions for size $l$ or for composition $\zeta$ are provided in Figure 2.

Turning to the amplitude of scattering of the degradation products, it is necessary to present the expressions for the elements of the structure matrix. To this end recourse should be made to the general expressions eqs 19 and 20 in which the functions eq 33 and/or eq 34 should be substituted depending on the type (eq 43) of

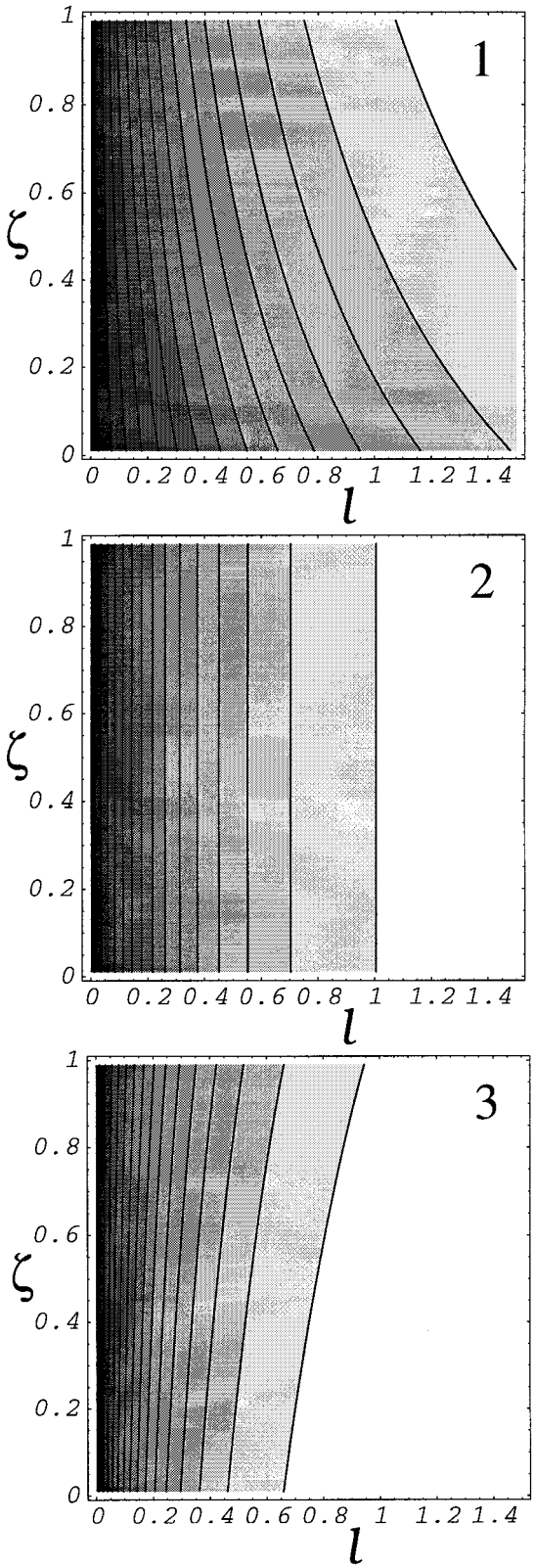


**Figure 1.** Contour plots (equal height lines) of the size ($l$)–composition ($\zeta = \zeta_1$) distribution (SCD) (eq 44) of degraded diblock copolymers of type III (double Flory distribution) at values of parameter $U = U_1 = k_1/(k_1 + k_2) = 1/10$ and initial composition $X = X_1 = {}^1/_3$ at rescaled times (eq 10) $\tau = 0$ (1), 1.19 (2), 2.38 (3). Darker regions correspond to larger probabilities.

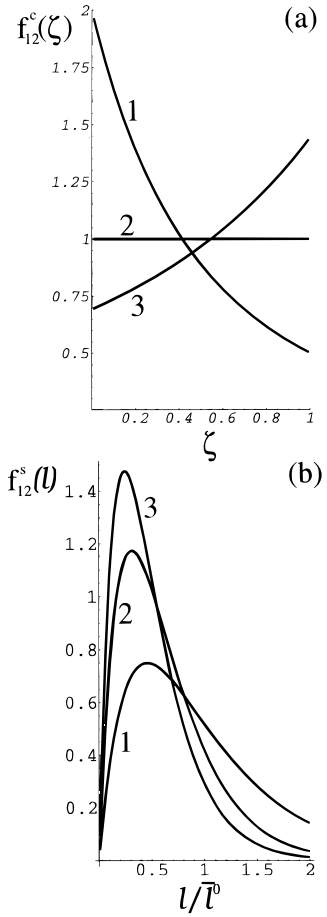


**Figure 2.** One-dimensional sections of size ($l$)−composition ($\zeta = \zeta_1$) distribution (SCD) (eq 44), describing the distribution for composition (a) and size (b) of degraded diblock copolymer of type III (double Flory). Values of the parameters $U$ and $X$ and rescaled times $\tau$ are the same as those presented in Figure 1, i.e, $U = {}^1/_{10}$, $X = {}^1/_3$, and $\tau = 0$ (1), 1.19 (2), 2.36 (3).

the initial block copolymer. In the case of type I, the formulas will bear resemblance to those derived earlier[16] concerning the phase behavior of monodisperse diblock copolymers

$$\tilde{X}_{\alpha\alpha}(y) = NX_\alpha^2 g(\hat{y}_\alpha)\ (\alpha = 1, 2), \quad g(x) = \frac{2}{x^2}(x - 1 + e^{-x}) \tag{51}$$

$$\hat{X}_{12}(y) = NX_1X_2h(\hat{y}_1)\ h(\hat{y}_2), \quad h(x) = \frac{1}{x}(1 - e^{-x}) \tag{52}$$

where the dependence of the variable $\hat{y}_\alpha$ on the wave vector modulus and time was determined above (eq 21). For the initial copolymers pertaining to type II we have

$$\hat{X}_{11}(y) = \bar{l}^0X_1^2g(\hat{y}_1), \quad \hat{X}_{22}(y) = 2\bar{l}^0X_2^2(1 + \hat{y}_2)^{-1} \tag{53}$$

$$\tilde{X}_{12}(y) = \bar{l}^0X_1X_2h\ (\hat{y}_1)(1 + \hat{y}_2)^{-1} \tag{54}$$

while for those of type III

$$\tilde{X}_{\alpha\alpha}(y) = 2\bar{l}^0X_\alpha^2(1 + \hat{y}_\alpha)^{-1}\ (\alpha = 1, 2) \tag{55}$$

$$\tilde{X}_{12}(y) = \bar{l}^0X_1X_2(1 + \hat{y}_1)^{-1}(1 + \hat{y}_2)^{-1} \tag{56}$$

The key problem to be investigated when considering "living" systems is the dependence on time of the quantity $H_m^{-1}$, which is the reciprocal of $H_m$ (eq 22). This quantity is equal to the ratio $T_m/\Theta$ of the maximum temperature $T_{max}$ for which the loss of thermodynamic stability of the homogeneous state happens to the Flory temperature $\Theta$. The temperature $\Theta$ is defined as the temperature at which the Flory−Huggings parameter $\chi$, describing the monomer−monomer interactions, reaches a value of a half. If during the degradation the value $T_{max}$ in its growth exceeds the temperature of the experiment $T$, the reaction system becomes absolutely unstable with respect to small composition fluctuations (spinodal decomposition).

Let us consider first the degradation of type I (eq 43) copolymer. In this case, the unit square of possible values of parameters $X_1 = X$ and $U_1 = U$ may be separated into three kinds of regions (Figure 3.I) concerning the shape of the curves characterizing the dependence of $T_{max}$ on the degradation time (see Figure 4). Whereas in the white region of Figure 3.I this dependence is monotonic, in the other two regions, gray and black, the function $T_{max}(\tau)$ has a maximum. The distinction between the latter two regions consists of the fact that in the gray area the Lifshitz point is situated to the right of the maximum, while in the black area it is located to the left of it. On the borderlines, dividing the regions of different colors, bifurcations of three types depicted in Figure 5 occur. Among them there is the nontrivial bifurcation occurring on the border between the white and the black regions at the intersection of which the location of the maximum of the curve $T_{max}(\tau)$ changes discontinuously from $\tau_m = 0$ (in the white region) to $\tau_m \neq 0$ (in the black region). When moving along the borderline $X = {}^1/_2$ from $U = 0$ to $U = {}^1/_2$ the time $\tau_L$ of reaching the Lifshitz point monotonically decreases from 5.778 to 3.785. An analogous decrease of $\tau_L$ takes place along the borderline between the gray and the black regions when within the interval $0.327 \leq X \leq {}^1/_2$ the quantity $\tau_L$ changes from 4.772 to 3.785. Along the third borderline, $U = {}^1/_2$, the character of the change of $\tau_L$ is analogous to that mentioned above; i.e., the value of $\tau_L$ decreases from $\infty$ to 3.785 as $X$ changes from 0 to ${}^1/_2$. The above-mentioned regularities of the behavior of $\tau_L$ at the borderlines of diagram I of Figure 3 are illustrated in Figure 6. In the point of intersection of all three borderline curves ($X = {}^1/_2$, $U = {}^1/_2$), the dependence $T_{max}(\tau)$ has the appearance shown in Figure 5, where $\hat{T}(0) = 100T_{max}(0)/\Theta\bar{l}^0 = 4.76$.

The diagram presented in Figure 3 allows us to predict the possible phase behavior of the products of the degradation of the type I block copolymers in the course of degradation at fixed temperature. If the values of the external parameters $X$ and $U$ are located within the white region of this diagram, the homogeneous state of the system remains locally stable for the whole period of degradation. When these parameters fall into the gray region of the diagram, there is a small interval $T_{max}(0) < T < T_{max}(\tau_m)$ of values of temperature where the system loses the stability of its homogeneous state at nonzero vector. Within the black region the above interval gets noticeably wider. Along with it there is, however, another temperature interval, $T_{max}(\tau_L) < T < T_{max}(\tau_m)$, where the system loses its stability at zero wave vector. In other words it can approach within the black region either the nontrivial or the trivial branch of the spinodal.

The dependence of the quantities $\tau_m$ and $\tau_L$ on $X$ is depicted in Figure 7. The value of $\tau_L$ is a smooth function

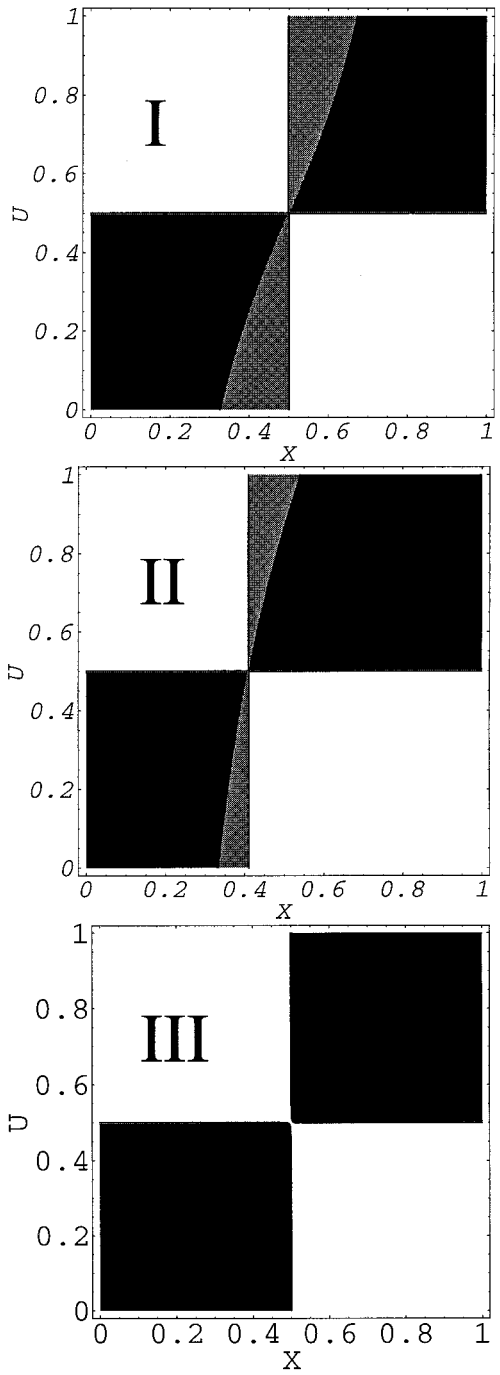


**Figure 3.** Classification diagram characterizing qualitative peculiarities of the dependence of the reduced temperature $\hat{T} = 100T_{max}/\bar{l}^0\Theta$ on the reduced degradation time $\tau$ for diblock copolymers of type I, II, and III (eq 43). Corresponding explanation is provided in the text and further illustrated in Figures 4−6.

of $X$, which diverges for $X \rightarrow 0$ *or* 1. The value of $\tau_m$, however, has a discontinuous derivative at the gray/black boundary, which is denoted by $X^*$, which is also the point where $\tau_m = \tau_L$. For $X > 0.5$ the value of $\tau_L$ is identically zero. The value of $X^* = 0.419$.

In Figure 8, the rescaled temperatures of phase separation at the times $\tau_m$, $\tau_L$ (depicted in Figure 7), and $\tau = 0$ are presented. The solid curve ($\hat{T}(\tau_m)$) will touch the long dashed curve ($\hat{T}(\tau_L)$) in one point ($X^*$) only and will be at higher $\hat{T}$ elsewhere. The long dashed curve lies very close to the solid curve for $X < X^*$, because from Figure 7 it is clear that $\tau_L$ and $\tau_m$ do not differ too much and Figure 4 demonstrates that the dependence of $\hat{T}$ on $\tau$ is rather weak around $\tau = \tau_m$. At rescaled temperatures above the solid curve phase separation

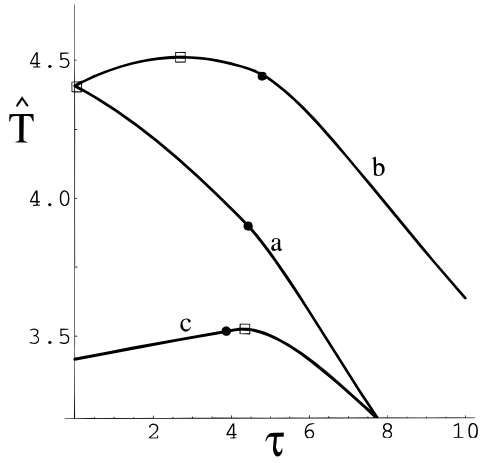


**Figure 4.** Reduced temperature $\hat{T}$ versus reduced degradation time $\tau$ (eq 10) in different regions of the classification diagram (Figure 3): white region (a), gray region (b), and black region (c). The point where the curve $\hat{T}(\tau)$ reaches its maximum value is denoted by an open square, whereas the Lifshitz point is represented by a filled circle. The curves presented in this figure are calculated for diblock copolymers of type I at the following values of the parameters: (a) $X = 0.4$; $U = 0.8$; (b) $X = 0.4$; $U = 0.1$; (c) $X = 0.3$; $U = 0.4$.

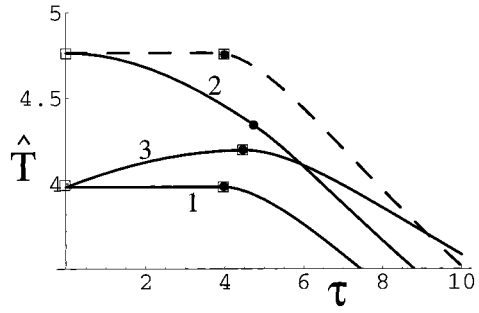


**Figure 5.** Dependence of the reduced temperature $\hat{T}$ versus the reduced degradation time $\tau$ on the boundaries between the different regions of classifications diagram 3.I. (1) white−black boundary ($X = 0.35$; $U = 0.5$) (2) white−gray boundary ($X = 0.5$; $U = 0.1$) (3) gray−black boundary ($X = 0.35$; $U = 0.1$) The dashed curve corresponds to the point ($X = 0.5$; $U = 0.5$) belonging to all three boundaries. The point where the curve $\hat{T}(\tau)$ reaches its maximum value is denoted by an open square, whereas the Lifshitz point is represented by a filled circle.

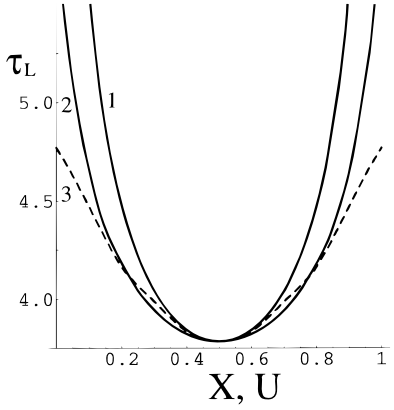


**Figure 6.** Values of the time of reaching the Lifshitz point $\tau_L$ along the boundaries between the regions of diagram 3.I. The numbering of the curves here correspond to those used for the designations of these boundaries in Figure 5.

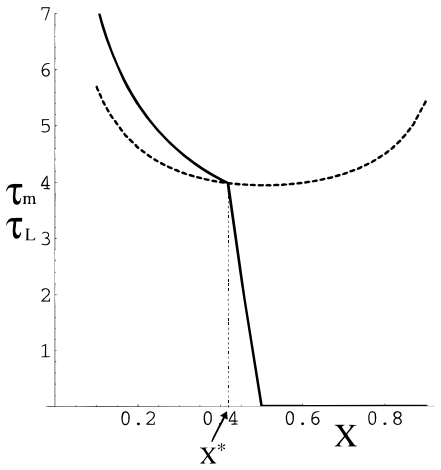


**Figure 7.** Dependence of the reduced time of reaching the maximum of the curve $\hat{T}(\tau)$, $\tau_m$ (solid line), and the Lifshitz point, $\tau_L$ (dashed line), on the composition ($X$) for diblock copolymers of type I. The curves were calculated with the parameter $U$ equal to 0.3.

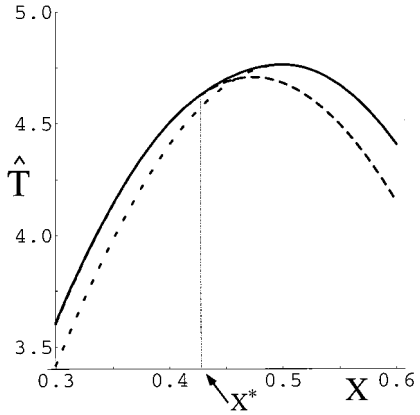


**Figure 8.** Dependence of $\hat{T}(\tau)$ at the points $\tau = \tau_m$ (solid line), $\tau = \tau_L$ (long dashed line), and $\tau = 0$ (short dashed line) on the composition of diblock copolymers of type I for parameter $U = 0.3$.

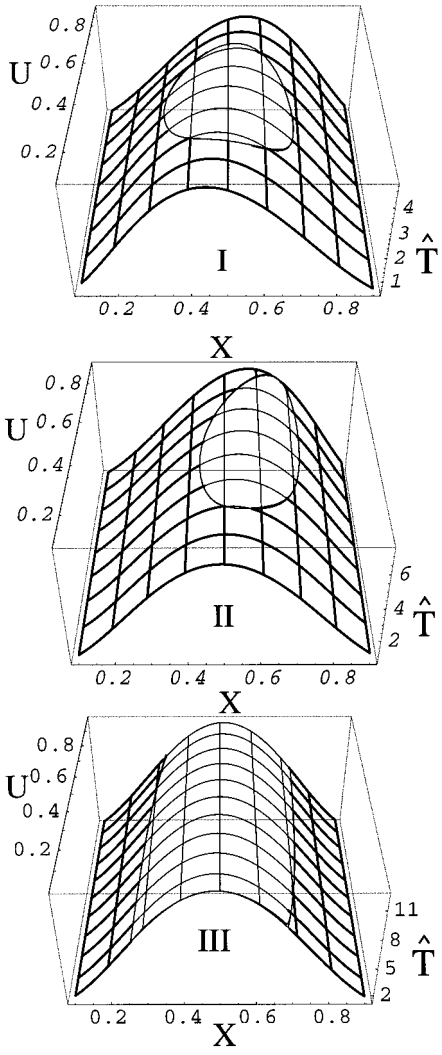


**Figure 9.** Examples of surfaces depicting the dependence of $\hat{T}$ on stoichiometric, $X$, and kinetic, $U$, parameters for the products of degradation of diblock copolymers of types I, II, and III obtained at values of the reduced degradation time $\tau = 4.0$ (I), $\tau = 1.6$ (II), and $\tau = 0.18$ (III). The trivial and nontrivial spinodal branches are indicated by thin and thick lines, respectively.

cannot be induced by destruction. For $X < X^*$, i.e., the black area, macrophase separation can be induced by destruction in the minute window of temperature separating the solid and the long dashed curve and for temperatures between the long dashed curve and the short dashed curve ($\hat{T}(\tau{=}0)$) microphase separation can be induced. For $X^* < X < 0.5$, i.e., within the gray area, only microphase separation can be induced if the rescaled temperature is between the solid and the short dashed curve. If $X > 0.5$, i.e., within the white area, no phase separation can be induced, because the short dashed curve and the solid curve are merged.

Under the degradation of block copolymers of type II the classification diagram (Figure 3.II) remains basically the same as for type I (Figure 3.I). The only qualitative distinction is the absence of symmetry with respect to the center of the square. On the borderline $X = 0.408$ between the white and gray regions the value $\tau_L(U)$ decreases from $\tau_L(0) = 1.956$ to $\tau_L(1/2) = 1.630$ and then increases to $\tau_L(1) = 2.621$. The same dependence takes place moving along the borderline separating the gray and the black regions where $\tau_L(0) = 2.000$, $\tau_L^{min} = \tau_L(0.622) = 1.607$, and $\tau_L(1) = 1.891$. On the borderline $U = 0.500$, the quantity $\tau_L(X)$ changing from $\tau_L(0) = \infty$ to $\tau_L(1)$ also goes through a minimum $\tau_L^{min} = \tau_L(0.575) = 1.502$. At the point ($X = 0.408$, $U = 1/2$) where the three boundary curves intersect $\tau_L = 1.629$.

The most simple diagram is shown in Figure 3.III corresponding to block copolymers of type III. It is symmetrical with respect to the center of the square and does not contain the gray region. On the vertical borderline $X = 1/2$ the value of $\tau_L$ is not influenced by $U$ and equals zero, while on the horizontal borderline $U = 1/2$ the quantity $\tau_L(X)$ monotonically decreases within the interval $0 \le X \le 1/2$ from $\tau_L(0) = \infty$ to $\tau_L(1/2) = 0$. As the analysis shows, under the degradation of diblock copolymer whose blocks are distributed exponentially, the width of the temperature interval where the system reaches the trivial branch of the spinodal during the degradation can be markedly higher than in the case of monodisperse blocks.

Up to this point, we were discussing thermodynamic stability of the spatially homogeneous state of a "living " system where the change of the size and composition of macromolecules occurs as a result of their degradation. Now let us consider the problem of the stability of a "dead " system representing the polymer melt composed of the products of the degradation of the block

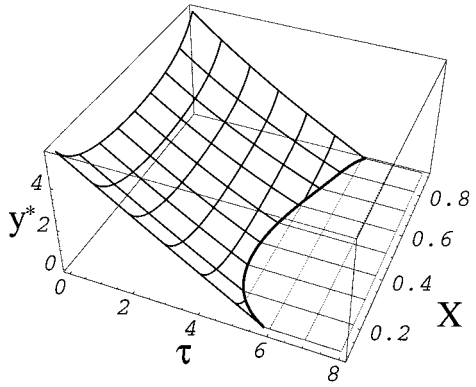


**Figure 10.** Surface portraying the dependence on composition and reduced degradation time of the reduced quantity $y^*$ (proportional to the square of the wave vector (eq 21)) at which the spinodal is reached when the degradation of type I diblock copolymers is stopped at time $\tau$. The value of the kinetic parameter $U = 0.1$.

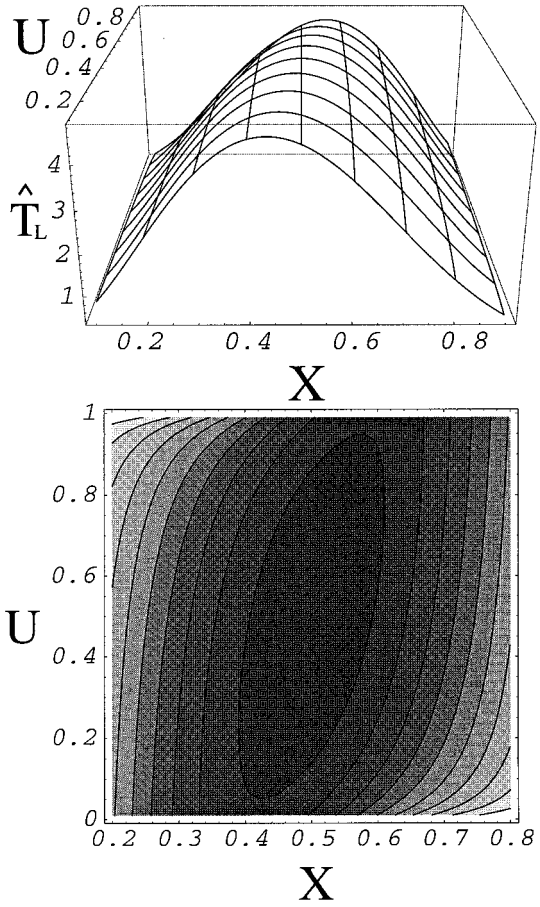


**Figure 11.** Surface of the reduced Lifshitz points $\hat{T}_L = \hat{T}(\tau_L)$ (a) and its contour plot (b) above the plane of parameters ($X$, $U$) for the products of the degradation of diblock copolymers of type I.

copolymers formed at a certain time of the degradation reaction. Apart from the initial parameters $X$ and $U$, the SCD of these products is entirely characterized by the dimensionless time $\tau$ of degradation of the initial block copolymers. At any fixed value $\tau$ it is possible to construct a surface describing the dependence of the reduced value $\hat{T}$ on $X$ and $U$ (see Figure 9). As can be seen, every spinodal surface presented in this figure comprises two regions composed of the points of trivial (top) and nontrivial (bottom) spinodal branches. These regions are separated by a line of the Lifshitz points

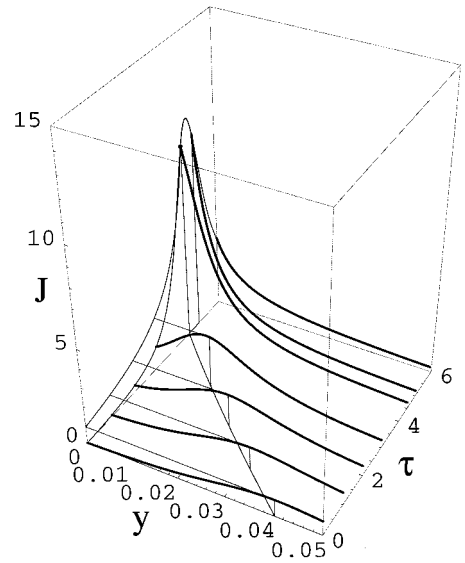


**Figure 12.** Evolution of the reduced scattering intensity (eq 11), $J = I/\{M(a_1 - a_2)^2\}$, of the products of degradation of diblock copolymers of type I, calculated at values of the parameters $X = 0.3$ and $U = 0.1$.

which appear at spinodal surfaces I, II, and III upon elapsed degradation time $\tau_I = 3.78$, $\tau_{II} = 1.50$, and $\tau_{III} = 0$. For block copolymers of the types I and II it happens at points $X_I = {}^1/_2$, $U_I = {}^1/_2$ and $X_{II} = 0.56$, $U_{II} = 0.58$ at values of $T_{max}$ equal respectively to 4.76 and 6.96. For the case of type III block copolymer the Lifshitz points fill the segment of the straight line $X_{III} = {}^1/_2$, $0 < U_{III} < 1$, $\hat{T} = 12.5$ already before the beginning of the degradation, so that the trivial branch of the spinodal surface will appear immediately.

Having the spinodal surface constructed, it is easy to indicate the temperature up to which the melt can be cooled without loss of thermodynamic stability of its homogeneous state as well as to answer the question whether this loss occurs at zero wave vector $q = 0$ or at one, distinct from zero $q = q^* \neq 0$. In the latter case, which corresponds to the nontrivial branch of the spinodal, of special interest is the value $q^*$ determining the period of the spatial structures of small amplitude formed under microphase separation.[16] Here recourse can be made to the theoretical results of the present work, such as those presented in Figure 10. By intersecting the surface depicted on this figure by planes $\tau = \tau_i$, the curves of the dependence $y^*$ on the composition of copolymer $X$ will be obtained. One of them, corresponding to $\tau_i = 0$, was presented already by Leibler.[16] Up to the moment $\tau = 4.47$, the curves $y^*(X)$ are situated entirely above the plane ($X$,$\tau$). Within the interval $\tau > 4.47$, the values $y^*$ are distinct from zero only on a portion of each of these curves. Evidently, the line along which the surface $y^*$ in Figure 10 intersects the plane ($X$,$\tau$) is nothing but the curve of the reduced time of attaining the Lifshitz points $\tau_L(X)$ (see Figure 6). The intersections of the above surface by the planes $X = X_i$ shows the character of the evolution of $y^*$ with time of the degradation $\tau$ of the block copolymer at given values of parameters $X$ and $U$. The character of the dependence of the temperature at the Lifshitz point $\hat{T}_L$ on the parameters $X$ and $U$ is depicted Figure 11.

The theory elaborated here allows us to find the amplitude of scattering $I(q)$ (eq 11) of the products of the degradation of block copolymer being formed at different times. Figure 12 illustrates the evolution of

this curve in the course of the degradation reaction. The position of the maximum shifts gradually to the region of small scattering angles whereas its height steadily increases. This happens up to a certain instant when the maximum of the curve $I(q)$ occurs at $q = 0$, to remain there for any later times of degradation.

## V. Conclusion

An important conclusion from this theoretical study is the existence of the possibility of phase separation in the melt of block copolymers subject to degradation. Depending on the values of kinetic and stoichiometric parameters, such a system can undergo either microphase or macrophase separation. The reason for this phenomenon is the growth (induced by chemical transformations) of the polydispersity for both size and chemical composition of the macromolecules involved. This factor should be taken into account when dealing with the processes of aging of block copolymer based materials.

## Appendix

When solving eq 2, let us take advantage of the fact that the independence of MWDs of the blocks of the initial copolymer molecules is retained during the degradation. Owing to this important property, the concentration of block copolymer molecules at any moment of time admits the factorization

$$C_{12}(l_1,l_2) = Y^0 f_1(l_1)\, f_2(l_2) \qquad \text{(A1)}$$

The evolution of the MWD of α-th type blocks, $f_\alpha(l_\alpha)$, is described by the solution of the following equation

$$\frac{1}{k_\alpha}\frac{\mathrm{d}f_\alpha(l_\alpha)}{\mathrm{d}t} = \int_{l_\alpha}^{\infty} f_\alpha(\xi)\,\mathrm{d}\xi - l_\alpha f_\alpha(l_\alpha)\ (\alpha = 1, 2) \qquad \text{(A2)}$$

where the function $f_\alpha(l_\alpha)$ at moment $t = 0$ is $f_\alpha^0(l_\alpha)$. Distributions $f_1(l_1)$ and $f_2(l_2)$ found in such a way will occur in the right-hand part of eqs 3 and 4, which being substituted into expression A1, will read

$$\frac{1}{k_\alpha}\frac{\mathrm{d}C_\alpha(l_\alpha)}{\mathrm{d}t} = Y^0\int_{l_\alpha}^{\infty} f_\alpha(\xi)\,\mathrm{d}\xi + 2\int_{l_\alpha}^{\infty} C_\alpha(\xi)\,\mathrm{d}\xi - l_\alpha C_\alpha(l_\alpha) \qquad (\alpha = 1, 2) \qquad \text{(A3)}$$

To solve the integro-differential equations (eqs A2 and A3) it is convenient to go from functions $f_\alpha(l_\alpha)$ and $C_\alpha(l_\alpha)$ to their Laplace transforms

$$g_\alpha(p_\alpha) \equiv \tilde{f}_\alpha(p_\alpha) = \int_0^{\infty} f_\alpha(l_\alpha)\exp(-p_\alpha l_\alpha)\,\mathrm{d}l_\alpha$$

$$\tilde{C}_\alpha(p_\alpha) = \int_0^{\infty} C_\alpha(l_\alpha)\exp(-p_\alpha l_\alpha)\,\mathrm{d}l_\alpha \qquad \text{(A4)}$$

in terms of which eqs A2 and A3 will turn into

$$\frac{1}{k_\alpha}\frac{\partial g_\alpha(p_\alpha)}{\partial t} = \frac{1}{p_\alpha}[g_\alpha(0) - g_\alpha(p_\alpha)] + \frac{\partial g_\alpha(p_\alpha)}{\partial p_\alpha} \qquad \text{(A5)}$$

$$\frac{1}{k_\alpha}\frac{\partial \tilde{C}_\alpha(p_\alpha)}{\partial t} = \frac{Y^0}{p_\alpha}[g_\alpha(0) - g_\alpha(p_\alpha)] + \frac{2}{p_\alpha}[\tilde{C}_\alpha(0) - \tilde{C}_\alpha(p_\alpha)] + \frac{\partial \tilde{C}_\alpha(p_\alpha)}{\partial p_\alpha} \qquad \text{(A6)}$$

To find the unknown functions $g_\alpha(0)$ and $\tilde{C}_\alpha(0)$ involved in the above equations, a transition to the limit $p_\alpha \to 0$ should be carried out in their right-hand parts. As a result, we will get 0 and $X_\alpha$ for eqs A5 and eq A6, respectively, which with allowance for initial conditions $g_\alpha^0(0)$ and $\tilde{C}_\alpha^0(0) = 0$ yields

$$g_\alpha(0) = 1 \qquad \tilde{C}_\alpha(0) = k_\alpha X_\alpha t \qquad \text{(A7)}$$

The solutions of the partial differential equations (eqs A5 and A6) with initial conditions $g_\alpha^0(p_\alpha)$ and $\tilde{C}_\alpha^0(p_\alpha)$ are obtained by means of the method of characteristics[17]

$$g_\alpha(p_\alpha) = \frac{\tau_\alpha}{p_\alpha + \tau_\alpha} + \frac{p_\alpha}{p_\alpha + \tau_\alpha}\, g_\alpha^0(p_\alpha + \tau_\alpha) \qquad \text{(A8)}$$

$$g_\alpha^h(p_\alpha) \equiv \frac{\tilde{C}_\alpha(p_\alpha)}{\tilde{C}_\alpha(0)} = \frac{\tau_\alpha}{p_\alpha + \tau_\alpha} + \frac{p_\alpha[1 - g_\alpha^0(p_\alpha + \tau_\alpha)]}{\bar{l}_\alpha^0(p_\alpha + \tau_\alpha)^2} \qquad \text{(A9)}$$

Performing in these formulas the inverse Laplace transform will result in expressions 8 and 9 for MWDs of types 1 and 2 blocks in a copolymer and MWDs of homopolymers, respectively. The knowledge of the first two of these distributions enables, proceeding from formula A1, to find the evolution of SCD $f_{12}$ ($l_1$, $l_2$) of the block copolymer molecules during their degradation.

The center $\bar{l}_\alpha$ and the dispersion $\sigma_\alpha^2 = \overline{l_\alpha^2} - \bar{l}_\alpha^2$ of the distribution for length $l_\alpha$ of α-th type block in a copolymer are easy to find by differentiating its generating function (eq A8) and setting $p_\alpha = 0$

$$\bar{l}_\alpha = \frac{1 - g_\alpha^0(\tau_\alpha)}{\tau_\alpha}, \quad \sigma_\alpha^2 = \frac{1}{\tau_\alpha^2}\{2\tau_\alpha g_\alpha^{0\prime}(\tau_\alpha) + 1 - [g_\alpha^0(\tau_\alpha)]^2\} \qquad \text{(A10)}$$

An analogous procedure being applied to the generating function of MWD of α-th type homopolymers enables to get simple expressions for their number-average degree of polymerization $P_{n\alpha}^h$ and polydispersity coefficient $K_\alpha^h$

$$P_{n\alpha}^h = \frac{1}{\bar{l}_\alpha^0\tau_\alpha}(\bar{l}_\alpha^0 - \bar{l}_\alpha),$$

$$K_\alpha^h \equiv \frac{P_{w\alpha}^h}{P_{n\alpha}^h} = \frac{2\bar{l}_\alpha^0[\bar{l}_\alpha^0 - g_\alpha^{0\prime}(\tau_\alpha) - 2\bar{l}_\alpha]}{(\bar{l}_\alpha^0 - \bar{l}_\alpha)^2} \qquad \text{(A11)}$$

Knowing the generating functions $g_1^0(p)$ and $g_2^0(p)$ of the distributions of blocks for length in the initial copolymers as well as their derivatives $g_1^{0\prime}(p)$ and $g_2^{0\prime}(p)$, it is not a serious problem to find the explicit dependence of the statistical characteristics (eqs A10 and A11) of the degradation products on time.

When $\tau_\alpha$ tends to zero in the right-hand part of the first formula A11, this latter is reduced to the relationship $P_{n\alpha}^h = P_{w\alpha}/2$, connecting the average degree of polymerization of homopolymers, being formed in the very beginning of the degradation, $P_{n\alpha}^h$, with that, $P_{w\alpha}$, which the blocks used to have in initial copolymer. Performing the limit $\tau_\alpha \to 0$ in the second formula A11 results in an analogous relation $K_\alpha^h = 4K_\alpha'/3$ between the polydispersity coefficients.

The above formulas enable to make two important conclusions. First, at sufficiently high polydispersity of block length in the initial copolymer, i.e., at $K_\alpha > 2$, their

average degree of polymerization, $P_{n\alpha}$, proves to be less than the average length of homopolymers, $P^h_{n\alpha}$, formed under the degradation of these blocks. The reason for this effect is due to the fact that polymeric chains with high molecular weights are more susceptible to degradation since the constant of this molecular reaction $k_\alpha l_\alpha$ grows with the length of block $l_\alpha$. The second essential conclusion consists of the answer to the question whether the MWD of homopolymers formed at the very beginning of the degradation of initial copolymer blocks is wider or narrower than the MWD of these latter. It turns out to be that the first case is realized if the ratio between polydispersity coefficients $K'_\alpha/K_\alpha$ is larger than $^3/_4$, while the second case takes place when this ratio is less than $^3/_4$.

When interpreting data obtained by a chromatographic experiment, the expression for the distribution of block copolymer molecules for their size $l = l_1 + l_2$ regardless of their composition can be of special interest. The generating function of such a one-dimensional distribution $f^s_{12}(l)$ can be obtained from the following expression

$$g_{12}(p) \equiv \int_0^\infty f^s_{12}(l) \exp(-pl)\, \mathrm{d}l = g_1(p)\, g_2(p) \qquad \text{(A12)}$$

where functions $g_1$ and $g_2$ have been determined above (eq A8). The $n$th-order statistical moment of distribution $f_{12}(l)$ is, evidently, equal up to the factor $(-1)^n$ to the derivative of the same order of the generating function $g_{12}(p)$ taken at point $p = 0$. Because the random quantities $l_1$ and $l_2$ are independent, the dispersion $\sigma^2_\alpha$ of their sum $l = l_1 + l_2$ will equal the sum of dispersions $\sigma^2_1$ and $\sigma^2_2$, where $\sigma^2_\alpha$ are defined by formula A10.

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