Kinetics of Phase Separation: Trapping of Molecules in Nonequilibrium Phases

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ABSTRACT: When solutions of molecularly nonuniform polymers in single solvents are rapidly (1 K/s) cooled into the two-phase region, up to 20% of the polymer mass and 1.5% of the solvent molecules that would be found in the more dilute phase (sol) under equilibrium conditions are instead found in the more concentrated phase (gel). The higher molecular weight material of the equilibrium sol is preferentially incorporated into the nonequilibrium gel, with a capture probability increasing linearly with log M. Qualitatively the observations can be explained by the following consideration: For high cooling rates the polymer coils shrink so rapidly that the mobility of some chains no longer suffices for their withdrawal from the overlap region with others in order to become part of the sol phase. Quantitative calculations performed on the basis of this concept demonstrate that all experimentally observed features can be well reproduced if two (measurable, but presently unknown) parameters are adjusted.

Introduction

Whenever it is attempted to separate macromolecules according to their chain length by means of the different solubilities, the maximum speed with which a second phase can be segregated without losing efficiency is one of the most serious questions. With all the different fractionation methods, like discontinuous precipitation, Baker–Williams fractionation,[1] or CPF[2] (continuous polymer fractionation), one is normally inclined to operate very slowly in order to be on the safe side, without knowing whether this is really necessary. The present work is therefore dealing with the influence of the rate of cooling (polymer solutions below their cloud points) on the composition of the coexisting phases. It is possible to limit the study to this variable, since one knows that nonequilibria are so metastable in the phase-separated systems of interest that the molecular weight distributions (mwd) of the polymers contained in the coexisting phases do not change detectably even within weeks.

The experimental procedure can be seen from Figure 1 for one of the systems under investigation. This graph shows the cloud-point curve for cyclohexane/poly(styrene) (M_w = 320 kg/mol, broad molecular weight distribution) and one coexistence curve, namely, that for a weight fraction, w_2° = 0.05, of the polymer in the starting solution. The inequality of the cloud-point curve and the individual coexistence curves results from the fact that the present systems are quasi-binary and that the molecular weight distribution of the polymer differs in the coexisting phases, except for the critical point. The Θ temperature of the particular system was in all cases chosen as the starting point, the two indicated end temperatures, T_1 and T_2, are both lower than the critical one. In the equilibrium cases the rate of cooling was on the order of 0.1 K/h (2.8 × 10^{-4} K/s); temperature jump experiments were carried out as rapidly as possible, which turned out to be approximately 1 K/s. Equilibrium (e) and nonequilibrium (ne) phases were analyzed with respect to their composition and to the subdivision of the polymer into the fractions (in terms of the total weight and that of individual polymer species).

It can be anticipated that differences between e and ne fractionation experiments show up as soon as the rate of cooling becomes so large that the disentanglement times of the polymer molecules can no longer guarantee the attainment of equilibrium at each temperature. In order to obtain information on the molecular mobility, some viscometric relaxation times were also measured in the temperature and concentration regime of interest.

Experimental Section

Materials. Poly(styrene) (PS) was kindly furnished by BASF (Ludwigshafen, West Germany); according to light scattering and GPC measurements it is a broadly distributed material (M_w/M_n = 2.5) with M_w = 320 kg/mol. All solvents were purchased from Merck (Darmstadt, West Germany). Cyclopentane (CP) and cyclohexane (CH) (both of UVASOL grade) were dried over molecular sieves and used without further purification. *trans*-Decalin (TD), for synthesis, was carefully rectified before use; the final content of the cis isomer as checked by gas chromatography amounts to less than 0.2%.

Phase Separation Experiments. Sufficient amounts of polymer solutions for the performance of both equilibrium and nonequilibrium experiments were prepared in closed cells and stirred for a minimum of 24 h, keeping the temperature higher than the corresponding θ temperature. The transfer into the glass cell shown in Figure 2 was accomplished with a syringe. The shape of the sealed vessel (containing ca 10 mL of solution) guarantees a rapid heat transfer and allows a very precise separation of the coexisting phases. Equilibrium experiments were carried out with a cooling rate of 0.1 K/h (programmable thermostat RKP 20 ± 0.02 K, of Lauda, West Germany) and most of the nonequilibrium measurements with the maximum attainable rate of 1 K/s (as determined by a thermocouple placed inside the vessel). Normally it took 1–14 days, depending on the particular system and concentration, until the phases became clear so that they could be separated. The sol (coexisting phase with the lower polymer concentration) was quantitatively withdrawn by using a syringe, and the remaining gel was, like the sol, diluted with toluene and poured into a surplus of methanol to precipitate the polymer. The sum of the weight of the polymers in the coexisting phases deviates from the initial mass in all cases on the order of 1%.

GPC Measurements. The molecular weight distributions of the fractions and of the starting polymer were obtained by means of a high-pressure gel permeation chromatograph (Waters, 4 Styragel columns, two 10^6 Å, one 10^5 Å, and one 10^4 Å). Tetrahydrofuran was used as the solvent; the concentration detectors were from Knauer, West Germany (UV), and Showadenko, Japan (RI). With use of standard polymers obtained from PSS (Mainz, West Germany), the calibration curve was represented by spline polynomials and used for the determination of the molecular weight distributions from the elution diagrams. The axial dispersion was checked and found to negligible for the width of distribution under consideration.

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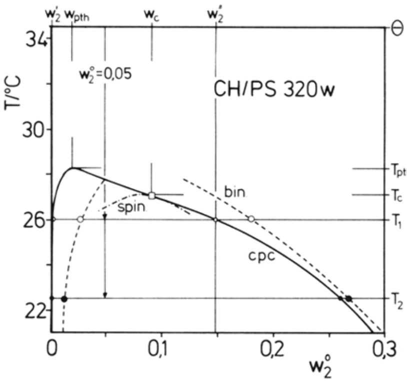

Figure 1. Phase diagram of the cyclohexane/poly(styrene) system (M_w = 320 kg/mol). The solid line represents the cloud-point curve and the dash-dotted one and spinodal curve. One binodal curve (broken line) is also given, namely, that for an overall concentration of the polymer, w_2° = 0.05. Θ, T_{pth}, T_c, T_1, and T_2 are the Θ temperature, the precipitation threshold, the critical temperature, and two end temperatures chosen for the present experiments.

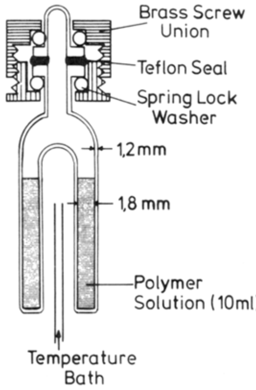

Figure 2. Sketch of the glass cell (not drawn to scale) used for the temperature jump and equilibrium experiments.

Rheology. Viscosity measurements were carried out on two rotational viscometers and attachments as supplied by Haake Messtechnik (Karlsruhe, West Germany). By using the measuring system NV (cup and bell-shaped rotors, gap width 0.4 mm) and the measuring heads MK 50 and MK 500, we can perform experiments up to a shear stress of approximately 10^4 Pa; the data for higher values were obtained with the measuring system HS I (cyclindric system, gap width 0.025 mm) and the measuring head MK 125. Both instruments were tested and calibrated with Newtonian oils. The evaluation of flow curves to obtain the characteristic viscometric relaxation times τ_0 was performed according to the Graessley–Ito theory on a computer as already described.[3]

Results

Phase Separation: Gross Effects. The most striking feature of nonequilibrium conditions is the trapping of polymer *and* solvent molecules in the gel phase. Figure 3 gives a generally valid scheme of the experimental findings: Although the absolute mass m_2'' of the polymer in the gel is always larger than under equilibrium conditions, the corresponding polymer concentration c_2'' (mass per volume) is less, due to the simultaneous capture of polymer and solvent molecules. The features displayed in Figure 3 remain valid in the case of molecularly uniform polymers, but the effects are less pronounced.

For quantitative considerations it is useful to compare W_2', the fraction of the total mass of the polymer contained in the sol phase. The equilibrium case can be seen from Figure 4, where W_2' is plotted as a function of the overall polymer concentration w_2° at different temperatures for the system CH/PS. As long as T remains below the critical temperature T_c, the curves start at the lower cloud-point concentration (where the entire polymer is still contained in the sol phase, i.e. W_2' = 1) and end at the higher (where the opposite is true, i.e. W_2' = 0). The critical line terminates at W_2' = 0.5, since the coexisting phases become identical at $T = T_c$ and $w_2 = w_{2c}$. For $T > T_c$, finally, the curves bend back and contract to a point (given by the polymer concentration w_{2pth} and temperature T_{pth} of the precipitation threshold) as T is raised.

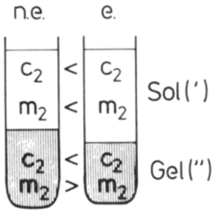

Figure 3. Qualitative comparison of phase separation in nonequilibrium (ne) and in equilibrium (e) experiments. m_2 and c_2 are the mass and the concentration (mass/volume) of the polymer in the less concentrated phase (sol, designated by a prime) and in the more concentrated phase (gel, designated by a double prime).

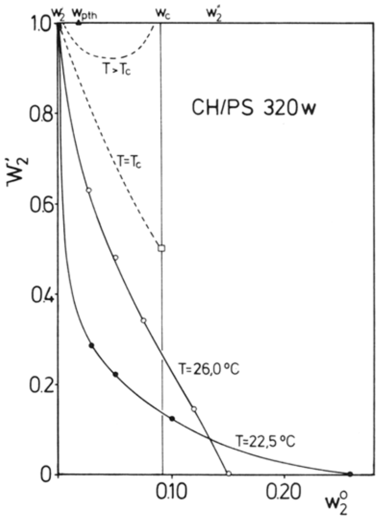

Figure 4. $W_2{}'_e$, the fraction of the total mass of the polymer contained in the equilibria sol phases, as a function of w_2°, the overall weight fraction of the polymer for the cyclohexane/poly(styrene) system (M_w = 320 kg/mol), and the indicated temperatures.

If one normalizes Δm_i, the mass of molecules of type i captured in the gel phase (identical with that missing in the sol phase)

$$\Delta m_i = m_i''{}_{ne} - m_i''{}_e = m_i'{}_e - m_i'{}_{ne} \qquad (1)$$

to the corresponding mass present in the equilibrium sol phase

$$\kappa_i = \Delta m_i/\mathrm{m}_i'{}_e \qquad (2)$$

the extent of ne effects can be measured by the capture parameter κ. The evaluation of data in terms of κ_i can be seen from Figure 5 for temperature jump experiments (1 K/s) performed with the same solutions for which the equilibrium behavior is shown in Figure 4.

Figure 5 demonstrates that up to ca. 1.5% of the solvent and up to ca. 20% of the polymer belonging into the equilibrium sol can be captured in the ne gel phase. When κ_i is plotted as a function of the overall concentration w_2° for isothermal conditions, one observes a maximum. These peaks are self-evident and result from fact that the amount of material transferred from one phase

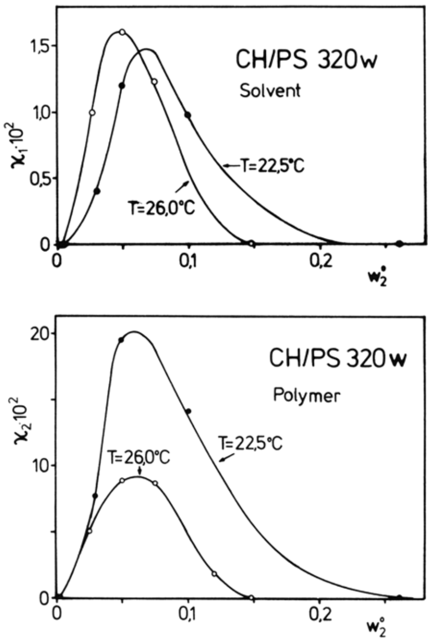

Figure 5. Variation of the capture parameter κ_i (eq 2) with w_2°, the overall weight fraction of the polymer, for the cyclohexane/poly(styrene) system (M_w = 320 kg/mol) and the indicated temperatures. Part a refers to the solvent and part b to the polymer.

Table I

solvent	η at $T = \Theta$, mPa	T_{pth}, °C	T, °C	$10^2 W_2{}'_{\text{e}}$	$10^2 \kappa_2$
CP	0.46	12.10	9.50	45.2	7.8
CH	0.77	28.20	26.00	48.0	8.9
TD	1.94	16.70	14.00	50.1	9.8

into another passes a maximum at intermediate w_2° values and that it is this transfer with which the capture of material is associated.

In order to check whether the viscosity η of the solvent influences κ_i to a measurable extent, cyclopentane (CP) and *trans*-decalin (TD) were also used as Θ solvents, in addition to CH. Some results with similar $W_2{}'_{\text{e}}$ values, i.e. a comparable fraction of the total polymer contained in the equilibrium sol phase, are collected in Table I.

According to these results the amount of trapped polymer increases noticeably as the solvent becomes more viscous: For CP the ne gel has caught ca. 8% of the polymer belonging into the e sol, but in the case of TD this percentage amounts to almost 10%. For two reasons this statement should, however, be considered only preliminary. First, the $W_2{}'_{\text{e}}$ values are not exactly identical so that it cannot be totally excluded that this is the factor which changes κ_2 and not η. Second, the displacement in the molecular weight distributions associated with the extent of trapping (cf. next section) did not yield clear-cut results. With all solvents the maxima of the GPC curves for the ne gels lie below the corresponding e value, as they should, but all to approximately the same extent (ca. 8%).

Phase Separation: Fractionation. The trapping of polymer molecules under ne conditions, which was discussed in terms of their total mass in the previous section, depends on chain length as demonstrated in Figure 6a for an experiment with the CH/PS 320w system at 22.5 °C, in which $W_2{}'_{\text{e}}$ was 0.22, i.e. for an approximately 1:4 distribution of the polymeric material onto sol and gel. From the GPC diagram it becomes obvious that the higher molecular weight components of the equilibrium sol are preferentially incorporated into the gel. This feature can also be seen from Figure 6b, which shows some results obtained with the TD/PS 320w system at 14.0 °C. For the chosen starting concentration of PS (3 wt %), the polymer in the equilibrium case is split evenly onto the two phases ($W_2{}'_{\text{e}}$ = 0.5). The distribution of the ne gel looks qualitatively very similar to that of the e distribution, but the maximum is shifted toward larger elution volumes; in other words, the average molar mass of the polymer in the gel is somewhat lower for the ne than for the e case.

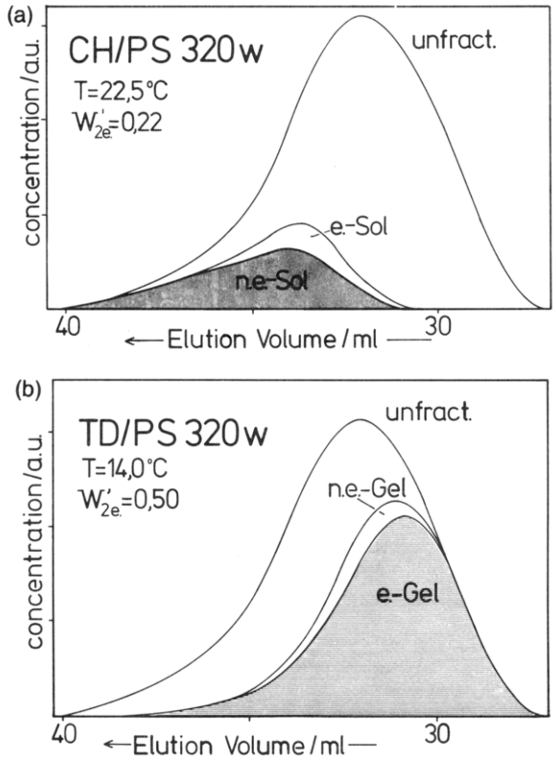

Figure 6. GPC diagrams for the initial polymer and for some fractions, taking into account W_2, the fraction of the total mass of the polymer contained in them. Part a: e and ne sol fractions for the cyclohexane/poly(styrene) system (M_w = 320 kg/mol) at 22.5 °C. Part b: e and ne gel fractions for the *trans*-decalin/poly(styrene) system (M_w = 320 kg/mol) at 14.0 °C.

The relative displacement δ of the mol wt M^{GPC}, corresponding to the maxima of the elution curves, in ne with respect to the e experiments can be used (by analogy with κ) to quantify this effect for either of the two phases:

$$\Delta M^{\text{GPC}} = M^{\text{GPC}}{}_{\text{ne}} - M^{\text{GPC}}{}_{\text{e}} \tag{3}$$

$$\delta = -\Delta M^{\text{GPC}} / M^{\text{GPC}}{}_{\text{e}} \tag{4}$$

Figure 7 gives the result for the sol phase of the CH/PS system and the lower end temperature. The maximum reduction of the mol wt is again observed at intermediate polymer concentrations and amounts to ca. 6%. A similar value (ca. 7%) is observed with the ne gel; the reason why a reduction of the average molecular weights takes place for both fractions is the following: The higher mol wt components of the sol captured by the gel in the ne experiments reduce not only the average of the gel since they are added on the low mol wt side of the distribution, but also that of the ne sol since they are removed from the high mol wt end of the e sol.

To study the influence of chain length j on the extent of capture of polymer molecules in the case of tempera-

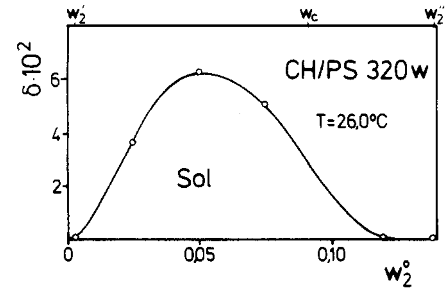

Figure 7. Relative diminution δ of the molecular weights corresponding to the maxima in the GPC elution curves in nonequilibrium experiments with respect to the equilibrium case (eq 4) as a function of $w_2°$, the overall weight fraction of the polymer for the cyclohexane/poly(styrene) system (M_w = 320 kg/mol) at 26.0 °C.

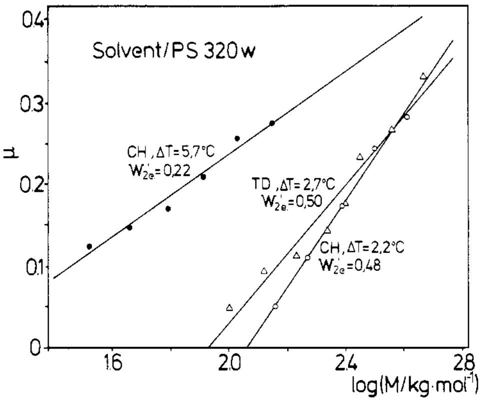

Figure 8. Probability μ that a molecule of molar mass M is captured in the gel phase (eq 6) as a function of log M for two experiments with the cyclohexane/poly(styrene) system (M_w = 320 kg/mol) and one with the same polymer but *trans*-decalin as the solvent. The magnitude of the temperature jumps, $\Delta T = T_{pth} - T$, and of $W_2'{}_e$, the weight fractions of the polymer contained in the corresponding equilibrium sol phases, are indicated in the graph.

ture jump experiments, GPC data were also evaluated according to

$$\Delta m_j = m_j''{}_{ne} - m_j''{}_e = m_j'{}_e - m_j'{}_{ne} \qquad (5)$$

$$\mu = \Delta m_j / m_j'{}_e \qquad (6)$$

μ represents the probability that a molecule of chain length j is captured. Figure 8 demonstrates that μ increases linearly with the logarithm of the polymer molecular weight. The molecular weight range of additional transfer varies with the particular conditions of fractionation.

Disentanglement Times. Since the molecular mobility of the individual polymer chains should govern the present ne effects, some accompanying rheological measurements were performed for CH/PS, the system of central interest. The obtained disentanglement times (characteristic viscometric relaxation times τ_o) are displayed in Figure 9 as a function of $w_2°$ for the Θ temperature and for the homogeneous region at 26 °C, one of the end temperatures under investigation. As expected from earlier measurements[4] with poly(n-alkyl methacrylates), the τ_o values increase exponentially with the polymer content of the solutions for constant T and range from 0.1 to 4 ms.

Discussion

Qualitative Considerations. First of all it is essential to exclude trivial reasons for the occurrence of the observed nonequilibrium phase separation behavior. The occlusion of parts of the sol phase in the gel phase or the freezing in of equilibrium states prevailing at higher temperatures could be such explanations. Both can, however, be dismissed on the basis of the present experiments with the molecularly nonuniform samples which demonstrate that the mwd of the polymer contained in the ne sol phase differs from that of any e sol phase. It is therefore necessary to search for other mechanisms. In order to simplify the reasoning, the following discussiong starts with the special case of molecularly uniform polymers, for which the principle phenomena, namely, the capture of polymer and solvent molecules in the gel phase, are the same as with the fractionation experiments.

The decisive experimental variable is $\dot{T}$, the rate of cooling, and one has to ask what changes can be provided by different $\dot{T}$ values within the still homogeneous and within the two-phase region. The disposable possibilities are discussed by means of Figure 10, where the (equilibrium) solubility gap of a polymer/solvent system is schematically given in terms of the reduced coil dimensions of the polymer, instead of the polymer concentration. At the Θ temperature all molecules are in

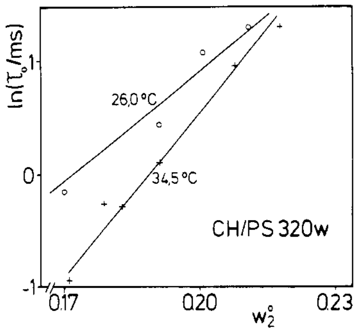

Figure 9. Disentanglement times τ_o as a function of $w_2°$, the overall weight fraction of the polymer for the cyclohexane/poly(styrene) system (M_w = 320 kg/mol) and the indicated temperatures.

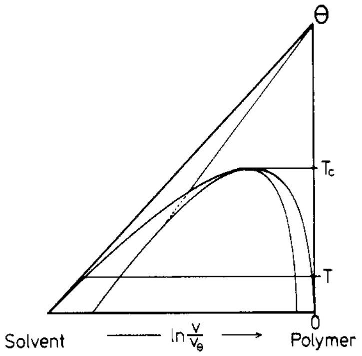

Figure 10. Generalized phase diagram of polymer–solvent systems in which the concentration variable is replaced by ln (v/v_Θ), where v is the volume a polymer coil occupies at a given composition of the solution and v_Θ its volume in the pure state (or at any concentration at the Θ temperature). If one assumes for simplicity that the relative change of v with T is constant, i.e. that ln (v) varies linearly with T, a solution of given composition can be characterized by a straight line passing through the vertex of this diagram, in which the right-hand limit represents the pure polymer and the left one the infinitely dilute solution. In equilibrium cooling experiments the lines end at the binodal curve where they split into two branches, one for the dilute and one for the concentrated coexisting phase of T-dependent composition. In nonequilibrium experiments, on the other hand, the lines transverse the metastable region (broken part) until they meet the spinodal curve where rapid decomposition takes place. From there on the system follows the boundary between the metastable and the instable region down to the end temperature T.

their unperturbed state, irrespective of the composition of the system, and the entire composition range has therefore degenerated into a point. As T is lowered, however, the coils shrink in the presence of solvent, and the more so, the lower the polymer concentration becomes. Within the limited temperature range of interest it is for the sake of simplicity assumed that the relative change of v_{coil} is proportional to T. This means that each solution of a given composition is represented by a straight line passing through the vertex of the modified phase diagram, which is on its right-hand side bound by the T axis (pure polymer) and on the left-hand side by ln (v/v_Θ) as a function of T for the infinitely dilute systems (pure solvent); v is the volume of the polymer coils.

If moderately concentrated solutions are cooled under equilibrium conditions, the coils shrink according to the polymer concentration until the solubility gap is reached and the phases begin to separate via nucleation and growth; at this temperature the lines split into two parts that proceed along the coexistence curve. In the case of large $\dot{T}$ values the question reads, how these paths change so that equilibria become unattainable. Concerning the lines situated within the homogeneous region it can be concluded from all one knows about the dynamics of polymer chains that the present $\dot{T}$ values are by far too low to change these paths, i.e. to displace the coil dimensions from their equilibrium value. The cooling rates under consideration should, however, be large enough to prevent the formation of phases via nucleation and growth.[5] In the case of sufficiently rapid quenching, the lines do no longer split as the demixing temperatures are reached but continue inside the miscibility gap (dotted line) until they hit the spinodal curve which they follow from there on. Now the phases separate via a spinodal mechanism or—if the spinodal line is not yet reached at the end temperature—via nucleation and growth from supersaturated solutions far from the corresponding binodal condition. It is obviously this situation that leads to the observed occurrence of nonequilibrium phenomena.

In order to rationalize why polymer and solvent molecules are captured in the gel phase in the case of temperature jump experiments, one has to think of the typical molecular processes associated with the attainment of equilibria. If a homogeneous polymer solution is decomposed into two phases of different composition, this implies a withdrawal of polymer and solvent molecules belonging to the sol phase out of the overlap region with other chains and the corresponding substitution of solvent/segment contacts by intersegmental contacts for the remaining polymer molecules forming the gel phase. In the present experiments, the above-mentioned segregation of a second phase is induced by cooling and this means that all coils shrink to an extent, given by the *local* composition of the system,[6] as the temperature is lowered. The fact that the concentration fluctuates widely as one approaches phase separation conditions (preformation of the coexisting phases) implies that coil shrinkage can locally take place even in the case of high overall polymer contents and that the withdrawal of macromolecules can still be considerably hindered even in the case of dilute systems.

As long as $\dot{T}$ remains small, the mobility of the polymer molecules suffices to attain equilibrium; i.e., all chains belonging to the sol phase can withdraw from the zone of overlap with other molecules. If, however, $\dot{T}$ is chosen so high that nucleation and growth far from the corresponding binodal temperature or spinodal decomposition take place, the rate of coil shrinkage and that of the withdrawal of chains from overlap regions becomes comparable. Under these conditions polymer molecules belonging to the sol phase are captured in the gel phase, and, together with them, also surrounding solvent molecules. The contribution of this ne process to the subdivision of the total material onto the two coexisting phases must obviously depend on the overall composition of the system such that it vanishes as all molecules accumulate in one phase and W_2' or W_2'' approaches zero.

Within the frame of the above picture, the experimental results obtained with molecularly nonuniform samples can be easily rationalized: The observed preferential capture of the higher molecular weight polymers which should be located in the equilibrium sol phase is due to fact that the rate of coil shrinkage goes up and that of withdrawal down (under else identical conditions) as the chain length is increased.

Model Calculations. For the subsequent considerations it is advisable to use a somewhat modified measure of the ne effects, instead of κ_i, defined by

$$\lambda_2 = \Delta m_2/m_2{}^\circ = W_2{}'_{\text{e}} - W_2{}'_{\text{ne}} \tag{7}$$

λ_2 normalizes the captured material Δm_2 to the total amount of polymer $m_2{}^\circ$, in contrast to κ_i, where this quantity is divided by $m_2{}'_{\text{e}}$, the material contained in the e sol phase. The reason for this change lies in the fact that λ_2, unlike κ_i, approaches zero automatically as one leaves the two-phase region. Furthermore, the ratio ρ of the rate constant k_{cs} for coil shrinkage and k_{wd}, that for their withdrawal from overlap regions, is introduced as a dimensionless variable

$$\rho = k_{\text{cs}}/k_{\text{wd}} \tag{8}$$

The rate constant for the shrinkage of coils can be represented by

$$k_{\text{cs}} = a_i\dot{T}\sigma \tag{9}$$

where

$$\sigma = (\partial \ln v_{\text{coil}}/\partial T)_{w_2{}^\circ} \tag{10}$$

The rate constant of the polymer withdrawal is taken to be inversely proportional to τ_{o}, the characteristic viscometric relaxation time

$$k_{\text{wd}} = a_2/\tau_{\text{o}} \tag{11}$$

The reduced variable ρ can therefore be rewritten as

$$\rho = a_3\dot{T}\sigma\tau_{\text{o}} \tag{12}$$

A mathematical relation for the dependence of λ_2, the normalized capture of polymers in the gel, on ρ and W_2' has to fulfill the following minimum requirements: It must approach zero as the cooling rate (and therefore also k_{cs} and ρ) is reduced or as practically all material remains in one phase (and W_2' is either unity or zero); furthermore, λ_2 has to approach finite limiting values for infinitely large cooling rates. Equation 13, in which A and B are constants, is the simplest expression that meets these conditions.

$$\lambda_2 = B\frac{A\rho}{1 + A\rho}W_2'(1 - W_2') \tag{13}$$

For the attempted model calculations it is necessary to know how ρ and W_2' vary with the weight fraction $w_2{}^\circ$ of polymer. In the case of W_2' this dependence is accessible from the experimental results and can be well described by

$$W_2' = 1 - ((w_2{}^\circ - w_2')/(w_2'' - w_2'))^{a_4} \tag{14}$$

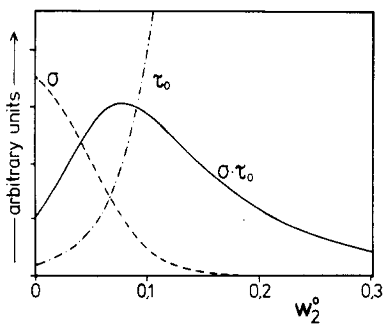

Figure 11. Calculation of the influence of the weight fraction $w_2{}^\circ$ of polymer on the coil shrinkage parameter σ [$= a_6(1 - \tanh(s(w_2{}^\circ - w_2{}^*)))$], on the disentanglement times τ_0 [$= \tau_0{}^\circ \exp(a_5 w_2{}^\circ)$] and on the product $\sigma\tau_0$, using the (realistic) parameters $a_5 = 40$, $w_2{}^* = 0.05$, and $s = 20$.

where a_4 is a constant ranging from 0.57 to 0.15 with the present experiments, depending on the value of T (cf. Figure 4). The ratio of the rate constants ρ contains two factors that vary with $w_2{}^\circ$, namely, σ and τ_0. For the latter quantity it is again possible to obtain the information from experiments. It can be written as

$$\tau_0 = \tau_0{}^\circ \exp(a_5 w_2{}^\circ) \qquad (15)$$

$\tau_0{}^\circ$ is the viscometric relaxation time at infinite dilution and a_5 a constant, the value of which decreases as T is lowered (cf. Figure 9).

With σ the situation is more difficult. The only information available in the literature concerns moderately concentrated polymer solutions for which it is stated that the coil dimensions vary with temperature according to a power law.[7] This dependence can, however, not be used for the present purposes since it implies that the coils shrink indefinitely upon going to infinite dilution, which would yield extremely large values of λ_2 for very low polymer concentrations in contrast to the experimental observation. For this reason a more realistic dependence is assumed, namely, that formulated in eq 16. This relation is characterized by a smooth transition of σ from a maximum value in the case of isolated coils down to zero for the pure polymer

$$\sigma = a_6(1 - \tanh(s(w_2{}^\circ - w_2{}^*))) \qquad (16)$$

For moderately concentrated systems the above dependence looks very similar to that resulting from the published exponential law. The parameter $w_2{}^*$ fixes the composition at which the transition from large to low T sensitivity of the coil dimensions takes place, and s measures its steepness.

The concentration dependences of σ, of τ_0, and of the product of these two quantities, which is decisive for the capture of polymer molecules during phase separation are depicted in Figure 11. In agreement with the experimental findings, $\sigma\tau_0(w_2{}^\circ)$ passes a maximum. At low concentrations the polymer chains are still mobile enough to escape, despite the large extent of coil shrinkage. At high concentrations, on the other hand, the temperature influence on the coil dimensions has become so small that even very slow molecules can get away.

Using the relations formulated in the eq 14–16, it is now possible to perform model calculation on the basis of eq 13. In doing so, it is assumed that the present cooling rates are still comparatively small so that $A\rho$ can be neglected as compared with unity so that this equation reduces to

$$\lambda_2 \approx C\rho W_2'(1 - W_2') \text{ for } A\rho \ll 1 \qquad (17)$$

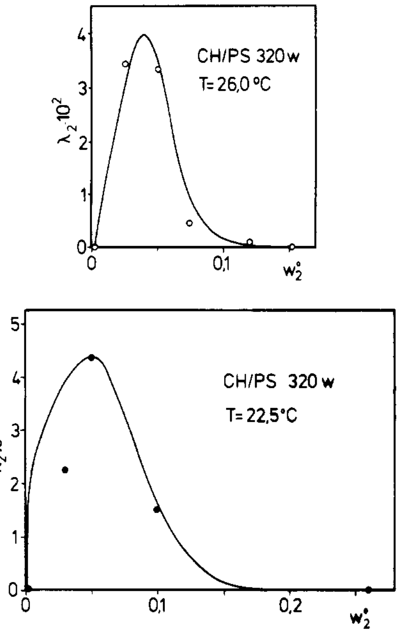

Figure 12. Polymer capture in the gel phase discussed in terms of λ_2 (eq 7) for the cyclohexane/poly(styrene) system (M_w = 320 kg/mol). Experimental data are given as open circles; the results of theoretical calculations performed on the basis of eq 17 are represented by full lines. All required parameters were taken from independent measurements, except for $w_2{}^*$ and s, which were adjusted such that the position of the maxima in $\lambda(w_2{}^\circ)$ and the shape of these curves are reproduced as good as possible. Part a: 26.0 °C, $a_4 = 0.57$, $a_5 = 33.8$, $s = 50$, $w_2{}^* = 0.045$. Part b: 22.5 °C, $a_4 = 0.15$, $a_5 = 27.6$, $s = 30$, $w_2{}^* = 0.062$.

The comparison of calculations performed on the basis of eq 17 with the present experimental findings is shown in Figure 12. Knowing the values of a_5 from viscosity measurements and that of a_4 from the equilibrium phase separation behavior, the parameters $w_2{}^*$ and s of eq 16 were adjusted such that the position of the maxima in $\lambda_2(w_2{}^\circ)$ are correctly reproduced. The constants a_3, a_6, and $\tau_0{}^\circ$ and the rate of cooling $\dot{T}$ are all contained in the constant C, the value of which was adjusted to the height of the maxima. Figure 12 demonstrates that the principle features of the concentration dependence of the capture of polymer molecules in the gel phase observed with temperature jump experiments can be well reproduced by the present model, if the two (so far unknown) parameters describing the coil shrinkage as a function of $w_2{}^\circ$ are adjusted. At the moment the reason for the exceptionally large deviation at 22.5 °C and the lowest $w_2{}^\circ$ value remains unclear; it could for instance be that the binodal decomposition or polymolecularity effects contribute more than usual under these conditions.

Of course it would be possible to perform analogous calculations for polymolecular samples if the appropriate molecular weight dependences are introduced in the relations 15 and 16; although such computations would be interesting in particular with the discussion of the observed preferential capture of the longer chains, they are postponed until more is known on $\sigma(w_2{}^\circ,M)$ and $\tau_0(w_2{}^\circ,M)$.

Conclusions

In the Introduction it was asked how quickly a second phase can be segregated in fractionation experiments without substantial loss of efficiency. On the basis of the present results the answer is the following: Although the separation of polymers according to their chain length does indeed become somewhat worse if the system is not allowed to attain equilibrium, the extent of the deterioration is not as pronounced as generally assumed, and the rate of changes in the thermodynamic conditions does obviously not play a decisive role.

The reason for this behavior lies in particular mechanisms of the nonequilibrium processes, which act in a favorable direction: As shown in Figure 8, long chains are preferentially incorporated in the ne gel, in a similar manner as they would be in equilibrium experiments at a somewhat lower temperature. With respect to fractionation, the effect is, however, not totally equivalent. This is due to the fact that the amount of material captured in the ne gel (cf. eq 6) increases linearly with the logarithm of the chain length, whereas the mass ratio of the individual polymer molecules contained in the coexisting equilibrium phases increases exponentially[8] with that variable.

Finally, some speculations appear worthwhile to be mentioned, namely, some interesting implications of the present findings for the discussion of the processes taking place in the preparation of polymer blends. If two-phase mixtures of polymer A and polymer B are prepared starting from homogeneous systems (e.g. by changing the variables of state or by evaporating a solvent) and equilibrium cannot be reached, molecules of polymer A will be captured in the phase rich in B and vice versa. This means that the concentration profile in the interfacial region of the segregated particles will change as if some compatibilizer (like a copolymer of A and B) were added, and this should bear consequences concerning the mechanical properties of the blend.

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References and Notes

(1) Baker, C. A.; Williams, R. J. P. *J. Chem. Soc.* **1956**, 2352.
(2) Geerissen, H.; Roos, J.; Wolf, B. A. *Makromol. Chem.* **1985**, *186*, 735.
(3) Ballauff, M.; Krämer, H.; Wolf, B. A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1217.
(4) Herold, F. Ph.D. Thesis, Johannes-Gutenberg-universität Mainz, 1985.
(5) Derham, K. W.; Goldsbrough, J.; Gordon, M. *Pure Appl. Chem.* **1974**, *38*, 97.
(6) Allegra, G.; Ganazzoli, F. *Gazz. Chim. Ital.* **1987**, *117*, 599.
(7) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Dublessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(8) Wolf, B. A.; Bieringer, H. F.; Breitenbach, J. W. *Br. Polym. J.* **1978**, *10*, 156.

Reptation in Semidilute Solutions of Wormlike Polymers

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ABSTRACT: We report fringe pattern fluorescence bleaching measurements of the self-diffusion coefficient of the wormlike polysaccharide xanthan at various molecular weights in aqueous solutions. Three distinguished concentration regimes are found: the dilute regime, the semidilute regime, and a new "concentrated" regime characteristic of wormlike polymers at concentrations where the intermolecular correlation length becomes smaller than the persistence length. We give simple scaling arguments that are consistent with the main trends in the data as a function of concentration and chain length and provide a fair estimate for the self-diffusion constant and the crossover concentrations.

Introduction

Understanding the motion of a polymer chain when surrounded by other (alike) polymer chains—such as occurring in semidilute polymer solutions or polymer melts—is of great fundamental and practical interest in polymer dynamics. Since the low-frequency rheological properties of such liquids are governed by the translational diffusion of the chains over distances large compared to the chain extension, much theoretical and experimental work has concentrated on the translational self-diffusion coefficient D_s measured on a macroscopic scale.[1-3] D_s depends on single-chain properties such as chain flexibility and chain length but also on interchain interactions and hence on the polymer concentration. In one of the prominent models proposed[4,5] to describe this a priori complex problem of statistical physics, one assumes that a given test chain "reptates" through the mess of surrounding chains. This means the test chain, being essentially confined at short times by the other chains into a curvilinear tube along its contour, has zero transverse diffusion and effectively propagates by one-dimensional diffusion along this contour. In the reptation model, predictions of D_s have been made for flexible chains in semidilute solutions and melts most easily by using simple scaling arguments.[6,7] The agreement with a large body of experimental data appears satisfactory now.[1] Reptation of rods has also been treated theoretically,[8-11] but a comparison with experiments appears

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