Distribution of Chemical Composition of Statistical Copolymers from the Conversion Dependences of Copolymer or Residual Monomer Mixture Composition

Jaroslav Stejskal,* Pavel Kratochvîl, Dagmar Straková, and Ondřej Procházka

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received January 22, 1986*

ABSTRACT: The average copolymer composition and residual monomer mixture composition for the statistical copolymerization of styrene and 2-methoxyethyl methacrylate (60 °C, AIBN) were followed as a function of conversion. A procedure of evaluation of the chemical composition distribution function using these experimental dependences is suggested. Methods of determination of chemical composition—differential refractometry in the case of copolymers and gas chromatography for monomer mixtures—have also been dealt with. Within the whole range of conversions, even under conditions of the gel effect, experimental data can be adequately described by relations derived from the classical copolymerization theory with two conversion-independent monomer reactivity ratios.

Introduction

Copolymer macromolecules are described by their molecular weight, chemical composition, and architecture, which involves the sequence arrangement of constitutional units and branching. The basic characteristics of a description of assemblies of such macromolecules are the distribution functions of molecular weight and chemical composition or their statistical moments.

The distribution function of chemical composition of binary statistical copolymers provides the most complete information on the composition of copolymer chains. It gains in importance especially in the case of chemically heterogeneous medium- and high-conversion copolymers. The distribution function may be obtained in three ways: (1) by calculation, assuming that a certain copolymerization theory holds within the whole range of copolymerization conversions; (2) by an analytical or preparative fractionation of the copolymer according to chemical composition, followed by characterization of the fractionated copolymer with respect to chemical composition; (3) by determination of the dependence of the average copolymer composition or of the composition of the residual monomer mixture on conversion.

The calculation of the chemical composition distribution (CCD) from the Mayo–Lewis copolymerization theory[1] is doubtless the easiest procedure. Skeist[2] has tackled this problem, but only the analytical relations derived later by Meyer and Lowry[3] were successfully applied on a major scale. Theoretical problems have been solved,[4] as well as those ensuing from practical requirements, e.g., in the design of gradient–index optics.[5]

According to the classical kinetic approach, the CCD is determined by only two kinetic parameters—the monomer reactivity ratios.[1,6] Deviations from the model behavior may be anticipated in a number of cases,[7] e.g., if the copolymerization takes place in a heterogeneous system[8] or via a more complex copolymerization mechanism.[9]

Recently, however, Johnson et al.[10] have expressed doubts as to the constancy of the monomer reactivity ratios at high conversions in the radical copolymerization of styrene and methyl methacrylate. A change in the monomer reactivity ratios was observed, particularly with the onset of the gel effect. The results of Johnson et al.[10] were reproduced by Dionisio and O'Driscoll.[11] A closer analysis of the system investigated in the latter papers reveals, however, that the choice of the starting composition of the monomer mixture (60 mol % styrene) probably is not the most suitable one for the investigation of changes in the chemical composition of the copolymer with conversion. The composition of the system under study approaches that of an azeotropic mixture; for the monomer reactivity ratios determined by Johnson et al.[10] at low conversions ($r_S = 0.56$ and $r_{MMA} = 0.44$) the azeotropic composition is ca. 56 mol % of styrene. Even small deviations in the experimentally determined copolymer composition from the theoretical prediction then apparently result in great changes in the monomer reactivity ratios. Teramachi et al.,[12] on the basis of an experimental determination of CCD for the same system, questioned the conclusion of Johnson et al., too. Teramachi et al.[13] also investigated the high-conversion copolymerization of styrene and methyl acrylate under conditions of gel effect. With respect to chemical composition, they did not find any deviations from predictions of the classical theory based on two reactivity ratios. A recent reexamination of the styrene—methyl methacrylate system by O'Driscoll et al.[14] and a critical evaluation of the preceding data led to an unambiguous conclusion that the classical copolymerization theory also applies to medium and high conversions. Hence, it has been one of the objectives of this study to check, using the copolymerization of sytrene and 2-methoxyethyl methacrylate as an example, to what extent the CCD calculated according to the classical theory reflects the physical reality.

Methods used in the fractionation of copolymers according to chemical composition and a critical evaluation of the results obtained have been reviewed by Inagaki and Tanaka.[15] In particular, the methods involve thin-layer chromatography,[12,13,16-18] high-performance liquid chromatography,[19,20] and other chromatographic methods.[21-25] The fractionation of copolymers in a simple solvent–precipitant system appeared to be of little efficiency.[26,27] An improved method, cross-fractionation, has been described in papers by Teramachi et al.,[28-30] already regarded as classical. The efficiency of this technique in the fractionation of copolymers according to chemical composition has been demonstrated in many cases.[26-32]

Little attention has been devoted to the third method of determining the CCD functions by following the copolymerization course, apparently because of the unsatisfactory sensitivity of the available analytical techniques. The conversion dependence of the average copolymer composition may be determined by repeated sampling at various conversions and by the determination of the composition of isolated copolymers by elemental analysis or NMR. Also, the composition of the residual monomer mixture may be monitored as a function of conversion by gas chromatography,[33] NMR,[14] and the like. The aim of

0024-9297/86/2219-1575$01.50/0

this study is to discuss the applicability of the conversion dependence of the average copolymer composition and of the composition of the residual monomer mixture to the determination of CCD.

Theoretical Section

Basic Relations. From the classical Mayo–Lewis theory[1] of the copolymerization of two monomers, A and B, Meyer and Lowry[3] and other authors[34,35] have derived a relationship between the instantaneous composition of the monomer mixture, y, expressed through the weight (or mole) fraction of component A and the weight (or mole) copolymerization conversion, ψ

$$\psi = 1 - \left(\frac{y}{y_0}\right)^{\alpha}\left(\frac{y-1}{y_0-1}\right)^{\beta}\left(\frac{y-a}{y_0-a}\right)^{\gamma} \tag{1}$$

where y_0 is the initial composition of the monomer mixture, $\alpha = r_B/(1 - r_B)$, $\beta = r_A/(1 - r_A)$, $\gamma = (r_Ar_B - 1)/[(1 - r_A)(1 - r_B)]$, and the parameter a has, for $0 < a < 1$, the meaning of the composition of the azeotropic copolymer, $a = t(1 - r_B)/[t(1 - r_B) + (1 - r_A)]$. r_A and r_B are the monomer reactivity ratios, and t is the ratio of molecular weights of the constitutional monomeric units of both types M_{0A}/M_{0B} if all compositions are expressed on weight basis. In the calculations performed in terms of mole fractions, we set $t = 1$.

The instantaneous copolymer composition, x, expressed again through the weight (or mole) fraction of component A, may be calculated from the copolymerization equation

$$x = \frac{y^2(r_A - t) + yt}{y^2[t(r_B - 1) + r_A - 1] + y(1 - 2r_Bt + t) + r_Bt} \tag{2}$$

The average composition $\bar{x}$, of a copolymer prepared up to the conversion ψ ensues from the material balance

$$\bar{x} = \frac{y_0 - (1 - \psi)y}{\psi} \tag{3}$$

If ψ_f denotes final conversion in a given copolymerization experiment, the ratio between the instantaneous and final conversion, ψ/ψ_f, is identical with the integral CCD function[3] of the copolymer, since it gives the fraction of macromolecules the composition of which is lower (at a suitable expression by the content of A or B) than that of the copolymer arising just at the conversion ψ.

The differential CCD function is then given by the definition

$$g(x) = \frac{1}{\psi_f}\left|\frac{d\psi}{dx}\right| = \frac{1}{\psi_f}\left|\frac{d\psi}{dy}\,\frac{dy}{dx}\right| \tag{4}$$

where the final conversion ψ_f plays the role of the normalization factor. The derivative $d\psi/dx$ is used in its absolute value, as it may be either positive or negative depending on the choice of the component used in expressing the composition x. By differentiation and using eq 1 and 2, Meyer and Lowry[3] obtained the explicit form of this distribution function expressed on the molar basis. Myagchenkov and Frenkel'[36] presented this function in a more general weight form

$$g(x) = \left|\left(\frac{y}{y_0}\right)^{\alpha}\left(\frac{y-1}{y_0-1}\right)^{\beta}\left(\frac{y-a}{y_0-a}\right)^{\gamma} \times \left(\frac{\alpha}{y} + \frac{\beta}{y-1} + \frac{\gamma}{y-a}\right) \times \frac{[y^2(r_Bt + r_A - 1 - t) + y(1 + t - 2r_Bt) + r_Bt]^2}{y^2(r_A + r_Bt^2 - 2r_Ar_Bt) + 2ytr_B(r_A - t) + r_Bt^2}\right| \tag{5}$$

where $y = y(x)$ according to eq 2. When using mole fractions, we again put $t = 1$.

Method of Calculation of Parameters for Medium- and High-Conversion Copolymerization. The calculation procedure suggested here is a modification of Kruse's method.[37]

All quantities concerned, i.e., the copolymerization conversion (ψ), composition of the copolymer just formed (x), average copolymer composition ($\bar{x}$), and the CCD function ($g(x)$), are expressed by eq 1–5 as functions of the composition of the residual monomer mixture (y). The actual independent variable in the experiment is the copolymerization conversion ψ, by means of which we would like to express the other parameters.

Consequently, in the calculation procedure y is changed gradually from the initial value y_0 toward higher or lower values. The direction of this change is estimated from the copolymerization diagram; if, e.g., a copolymer is formed that contains a higher fraction of component A than the corresponding monomer mixture, the latter becomes poorer in this component and y decreases. From eq 1 we calculate the corresponding conversion ψ. The procedure is repeated until the conversion reaches the required value, e.g., the experimental one. The remaining parameters x, $\bar{x}$, and $g(x)$ are calculated from eq 2–5 by using the known ψ and the corresponding y.

Determination of the Distribution Functions of Chemical Composition from Conversion Dependences of the Average Copolymer or Residual Monomer Mixture Composition. In order to determine the differential CCD function $g(x)$ by means of eq 4, one must know the dependence of the instantaneous copolymer composition x on conversion, i.e., $x(\psi)$. This dependence is monotonic; therefore, there exists its inversion function, $\psi(x)$, for which we have

$$\frac{d\psi(x)}{dx} = \left(\frac{dx(\psi)}{d\psi}\right)^{-1} \tag{6}$$

A procedure leading to the direct determination of the dependence $x(\psi)$ has not yet been suggested. Experimentally, however, it is possible to determine the conversion dependence of the average copolymer composition $\bar{x}(\psi)$ or the monomer mixture composition $y(\psi)$. The two latter dependences bring identical information because they obey the balance condition (eq 3).

A similar dependence for the instantaneous copolymer composition can be calculated[11] from the conversion dependence of the average copolymer composition $\bar{x}(\psi)$:

$$x(\psi) = \bar{x}(\psi) + \psi\frac{d\bar{x}(\psi)}{d\psi} = \bar{x}(\psi) + \frac{d\bar{x}(\psi)}{d\ln\psi} \tag{7}$$

By combining eq 7 and the balance condition (eq 3), it is possible to obtain the relationship between the instantaneous copolymer composition, $x(\psi)$, and the monomer mixture composition, $y(\psi)$,

$$x(\psi) = y(\psi) - (1 - \psi)\frac{dy(\psi)}{d\psi} = y(\psi) + \frac{dy(\psi)}{d\ln(1 - \psi)} \tag{8}$$

without any assumptions regarding the copolymerization kinetics.

When treating experimental data according to eq 7 or 8, it is always difficult to obtain the derivative $d\bar{x}(\psi)/d\psi$ or $dy(\psi)/d\psi$ with sufficient accuracy; in the calculation of the distribution function $g(x)$ further differentiation according to eq 6 reduces the accuracy still further. Along with subjective graphic treatment, there exist two other possible calculation procedures: (a) plotting a smooth empirical curve through all experimental points, e.g., a polynomial of the *n*th degree, followed by an analytical calculation of the derivatives; and (b) smoothing out experimental data piecewise and calculating the corrected functional value and derivative for each point separately; it is advisable to repeat the procedure once or twice, depending on the number of points used in this procedure. Both methods are examined below.

Experimental Section

Preparation of Copolymers. Styrene was a commercial product of Lachema, Czechoslovakia. 2-Methoxyethyl methacrylate (MEMA) was prepared[38] by esterification of methacrylic acid with 2-methoxyethanol (methyl cellosolve). Both monomers were redistilled on a laboratory column, and their purity (99.7 and 99.8 wt %, respectively) was checked by gas chromatography. Initiator, azobis(isobutyronitrile) (AIBN), was recrystallized twice from methanol. Benzene, reagent grade quality (Lachema, Czechoslovakia), was used without further treatment.

The monomer mixture containing the initiator and benzene (if used) was bubbled with nitrogen and sealed into several ampules. These were thermostated to 60 °C. The individual ampules were taken after chosen time intervals, and their contents were precipitated into an excess of methanol. Samples prepared to high conversion were first diluted in cold benzene. The copolymers were reprecipitated from benzene solution into methanol, separated, and dried in vacuo at 90 °C, and their conversion was determined by weighing.

Copolymer Composition. The chemical composition of copolymers was determined by elemental analysis and differential refractometry.[39] In the differential refractometric method, the difference is determined of the refractive indices between the copolymer solution and that of a reference sample (again, one of the copolymers). It can be demonstrated[39] that this difference is proportional to that between the chemical compositions of the measured and reference copolymer. In this procedure, it is useful to choose the solvent and the reference copolymers with the smallest possible difference between their refractive indices.[39] The copolymer concentration in solution depends on the required accuracy of the difference in chemical compositions to be determined, which we chose to be ~0.1 wt % styrene.

The refractive index differences of 5 wt % copolymer solutions in 1,2,4-trichlorobenzene with respect to a solution of the reference sample of the same concentration were determined by using a Brice-Phoenix, Model BP-2000-V, differential refractometer. The corresponding differences in the chemical composition of the copolymers were then calculated from the refractive index differences. The refractive index increments, d*n*/d*c*, of the individual homopolymers were +0.028 cm^3/g for polystyrene and −0.067 cm^3/g for poly(2-methoxyethyl methacrylate) (PMEMA) (25 °C, 546 nm). The refractive index increments of the reference copolymer (68.5 wt % styrene) was −0.002 cm^3/g.

Composition of the Residual Monomer Mixture. Some ampules were cooled after polymerization, and their content was diluted to 80 vol % benzene in all cases.

The solutions were injected into a gas chromatograph, and the composition of the residual monomer mixture was determined from the ratio of areas of the detected peaks of styrene and MEMA. The results thus obtained were poorly reproducible and depended on the operational conditions, probably due to the sorption of monomers by the polymer[40] or the degradation of polymer residues on the evaporator of the apparatus.

For this reason, the benzene solutions were mixed with the same volume of *n*-heptane. The copolymer precipitated, and clear supernatant was injected into the chromatograph. Although this led to a dilution of the monomer mixture and to the introduction of another component into the mixture, reproducibility of determination of the composition of the monomer mixture improved considerably (to about 0.5 wt % styrene) and was independent of the operational regime of the apparatus.

Calibration was performed by analyzing the monomer mixture of known composition in which the copolymer had been dissolved so as to simulate conditions corresponding to a 10–90 wt % copolymerization conversion. The calibration solutions were also diluted with benzene, after which the copolymer was precipitated with *n*-heptane. The relationship between the ratio of the peak areas and the composition of the monomer mixture was independent of the copolymer content within the whole range of simulated conversions.

Table I
Initial Molar Concentration of Initiator ($[I]_0$) and Total Molar Concentration of Monomers ($[M]_0$) for Copolymerization of Styrene and 2-Methoxyethyl Methacrylate in Benzene[a] Conducted to Weight Conversion ψ_f

run	benzene, vol %	$[I]_0$, mol/L	$[M]_0$, mol/L	$[I]_0^{1/2}[M]_0$	ψ_f
I[b]	0	4.0×10^{-4}	8.28	0.166	0.98
II[b]	0	1.6×10^{-3}	8.28	0.331	0.99
III	50	1.6×10^{-3}	4.14	0.166	0.53
IV	80	1.6×10^{-3}	1.66	0.066	0.40
V	80	1.0×10^{-2}	1.66	0.166	0.86

[a] Initial composition of monomer mixture 76.7 wt % (=82.0 mol %) styrene in all cases. [b] The upward bend on conversion–time curves, interpreted as the onset of gel effect, has been observed at conversions 0.32 (run I) and 0.28 (run II).

Results and Discussion

Survey of the Results. The properties of statistical S-MEMA copolymers were investigated by us earlier.[26,32,41] This is why this particular pair of monomers, much resembling the pair styrene–methyl methacrylate from the kinetic point of view, has been chosen also for the present study.

Five runs of copolymers with different concentrations of initiator and benzene as diluent were prepared (Table I). In all cases the starting composition of the mixture of monomers was 76.7 wt % (i.e., 82.0 mol %) styrene; at such composition, the maximal difference may be anticipated between the copolymer composition and that of the monomer mixture at the onset of copolymerization. In three cases, the copolymerization proceeded at the same starting initiator concentration (runs II–IV); in three cases it was also carried out at the assumed equal starting rate of monomer consumption (runs I, III, V).

Correlation between the experimental results and the theoretical prediction is graphically shown in Figure 1 and, for run V along with further data, in Figures 2 and 3. The theoretical conversion dependences of the average copolymer composition and of the monomer mixture composition were calculated by a procedure based on the study by Meyer and Lowry[3] for the monomer reactivity ratios $r_S = 0.46$ and $r_{MEMA} = 0.48$, which best fit the experimental data. Within the limits of experimental error, these values coincide with data obtained earlier for low-conversion copolymerizations,[41] $r_S = 0.41$ and $r_{MEMA} = 0.48$.

Figure 2 illustrates to what extent the theoretical prediction is affected by the choice of the monomer reactivity ratio values. In a system rich in styrene, which corresponds to our case, the conversion dependence of composition is predominantly determined by the reactivity ratio of styrene, the influence of the other parameter being less significant. The average copolymer composition depends on the monomer reactivity ratios mainly in the range of low conversions; for high conversions, the average copolymer composition approaches the starting composition of the monomer mixture and remains virtually unaffected by the values of the monomer reactivity ratios. A composition between the two analytical methods, i.e., elemental analysis and differential refractometry,[39] in the determination of the average copolymer composition shows that the differential refractometry provides data basically identical with those provided by the other analytical method with

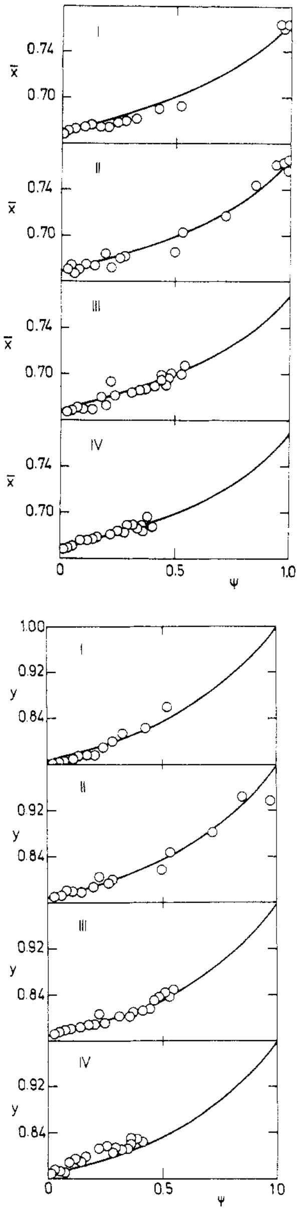

Figure 1. Dependence of the average copolymer composition ($\bar{x}$) and the residual monomer mixture composition (y) (both given by the weight fraction of styrene) on the weight conversion (ψ) for runs I–IV compared with the theoretical prediction for r_S = 0.46 and r_{MEMA} = 0.48 (solid line).[42]

a smaller scatter of experimental data.

For the investigation of copolymerization above a certain conversion (this conversion depending on the particular reaction conditions), it is in principle more suitable to determine the composition of the residual monomer mixture. The latter is little dependent on the monomer reactivity ratios in the range of low conversions but becomes sensitive to their values at larger conversions (Figure 3). A certain problem exists in the fact that at high conversions the residual amount of monomer mixture is low, and its analysis may be difficult, which has been the case in the present study.

From a comparison of the conversion dependences of the average copolymer composition and residual monomer mixture composition with those theoretically predicted (Figures 1–3), it may be concluded that the classical theory of copolymerization assuming two constant values of the monomer reactivity ratios can adequately describe, within the limits of experimental error, these two dependences in the whole range of conversions, even if the gel effect is operative (runs I and II).

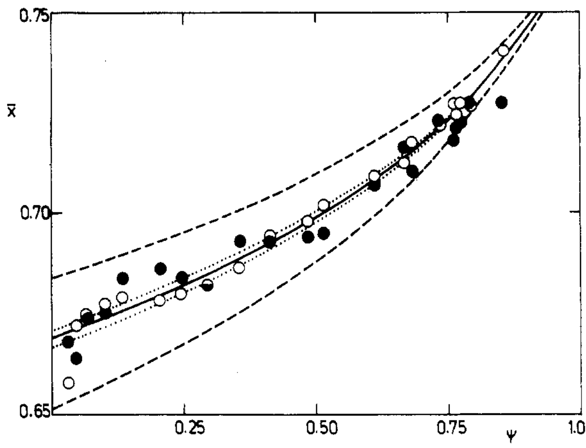

Figure 2. Dependence of the average copolymer composition $\bar{x}$ (weight fraction of styrene), determined by differential refractometry (○) and elemental analysis (●), on the weight conversion ψ for run V and its comparison with the theoretical prediction for r_S = 0.46, r_{MEMA} = 0.48 (solid line); r_S = 0.46 ± 0.05, r_{MEMA} = 0.48 (broken line); and r_S = 0.46, r_{MEMA} = 0.48 ± 0.05 (dotted line).[42]

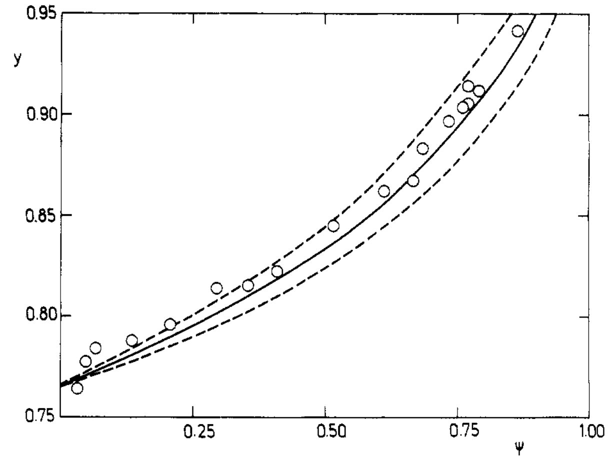

Figure 3. Dependence of the residual monomer mixture composition y (weight fraction of styrene) on the weight conversion ψ for run V and its comparison with the theoretical prediction for r_S = 0.46, r_{MEMA} = 0.48 (solid line) and r_S = 0.46 ± 0.05, r_{MEMA} = 0.48 (broken line).[42]

Determination of Chemical Composition Distribution. Using the results of copolymerization V (Figures 2 and 3),[42] we illustrate the feasibility of determination of the differential CCD function by a procedure suggested in the Theoretical Section. The experimental conversion dependence of the average copolymer composition, $\bar{x}(\psi)$, and of the instantaneous composition of the residual monomer mixture, $y(\psi)$, were approximated by a polynomial of nth degree using the least-squares method. Thus

$$\bar{x}(\psi) = \sum_{k=0}^{n} a_k \psi^k \qquad (9a)$$

$$y(\psi) = \sum_{k=0}^{n} b_k (1-\psi)^k \qquad (9b)$$

where a_k and b_k are the kth polynomial coefficients. According to eq 7 and 8, the conversion dependence of the instantaneous composition reads

$$x(\psi) = \sum_{k=0}^{n} (k+1) a_k \psi^k \qquad (10a)$$

or

$$x(\psi) = \sum_{k=0}^{n} (k+1) b_k (1-\psi)^k \qquad (10b)$$

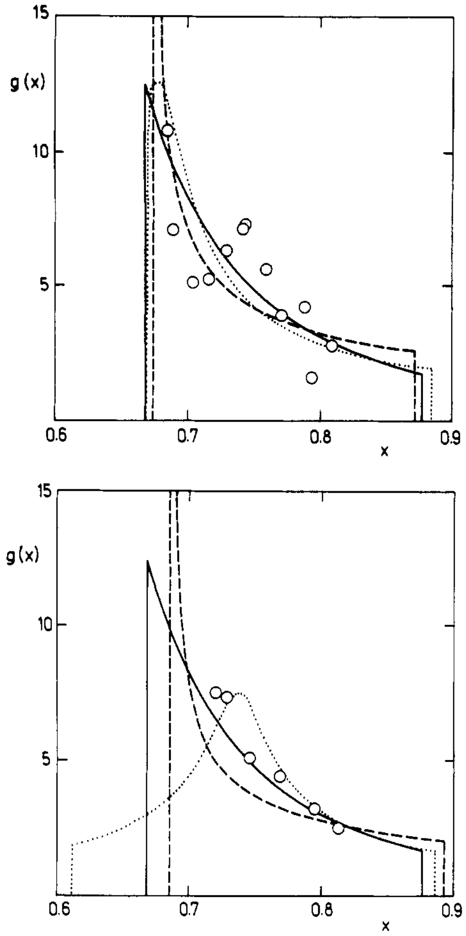

Figure 4. Differential distribution function $g(x)$ of the chemical composition of the copolymer prepared to conversion $\psi_f = 0.86$ (run V, cf. Table I) evaluated from the experimental conversion dependence (top) of the average copolymer composition and (bottom) of the residual monomer mixture composition. The distribution functions have been calculated from the approximation of conversion dependences by a polynomial of the second (broken line) and third (dotted line) degree and compared with the theoretical prediction for the monomer reactivity ratios $r_S = 0.46$ and $r_{MEMA} = 0.48$ (solid line). Points (○) denote discrete values of the distribution function obtained by piecewise fit.

and for its derivative, which according to eq 4 is proportional to reciprocal values of the CCD function, we obtain

$$\frac{dx}{d\psi} = \sum_{k=0}^{n} k(k+1)a_k\psi^{k-1} \tag{11a}$$

or

$$\frac{dx}{d\psi} = \sum_{k=0}^{n} k(k+1)b_k(1-\psi)^{k-1} \tag{11b}$$

The calculation was performed for $n \geq 1$ while watching the point when the average standard deviation would cease to decrease significantly. Both for $\bar{x}(\psi)$ and $y(\psi)$, it was found that the difference between the magnitudes of standard deviations for $n = 2$ and $n = 3$ were on the boundary of significance. We therefore present the results of both the quadratic and cubic approximations (Figure 4). In piecewise fit, a straight line was drawn through each set of five adjacent experimental points by the least-squares method; for the middle point, its value and derivative in this point were calculated. By use of these values, and eq 7 and 8, x was calculated; further piecewise fit gave x and $dx/d\psi$, from which the values of the distribution function $g(x)$ in discrete points x were evaluated (Figure 4). Basically, such procedure can also adequately reflect sudden changes in the course of the dependence (e.g., a sharp bend), unlike the case where a polynomial function is drawn through all experimental points. Since the calculation of x and $g(x)$ involves the use of derivatives, experimental errors of the individual points play a much more pronounced role, which somewhat reduces the practical significance of the method of piecewise fit. A further disadvantage of the latter method is that the marginal parts of the distribution function are not defined because, with such treatment of experimental data, we lose marginal points on either side.

It follows from eq 7 and 8 that the accuracy of determination of x and $g(x)$ from $x(\psi)$ should be highest at low conversions and, conversely, for x and $g(x)$ determined from $y(\psi)$, at high conversions.

The distribution function $g(x)$ calculated from the plot of the conversion dependence of the average copolymer composition according to eq 9 by the polynomial of the second, and especially of the third, degree fits well the theoretical dependence (Figure 4, top). The $g(x)$ values in the discrete points x obtained by piecewise fit of the experimental dependence also agree tolerably with the predicted course.

The distribution function $g(x)$ calculated from the approximation of the conversion dependence of residual monomer mixture composition by the polynomial of the third degree adequately copies the theoretical dependence, as expected, in the range of higher x (Figure 4, bottom). On the other hand, it differs from the theoretical prediction in its width and course in the range of lower x values (i.e., at low conversions). The reason is seen in the fact that the cubic plot—unlike the quadratic one—can follow the downward bend in the conversion dependence in the initial stage of copolymerization (Figure 3), which may not have any physical meaning. A very good fit with the theoretically predicted $g(x)$ is observed for points obtained by smoothing out experimental data by parts (Figure 4, bottom).

Estimates of the differential distribution function of chemical composition $g(x)$ obtained by the described procedures are certainly subject to a considerable experimental error. In spite of this, however, the accuracy of such determination of the CCD function is much better than if, with the unsatisfactory state of separation techniques available at present, the distribution function were determined directly by one of the fractionation procedures.

Acknowledgment. We thank Mrs. E. Plachetková for chromatographic analyses of monomer mixtures.

Registry No. MEMA, 6976-93-8; styrene, 100-42-5; (styrene)·(MEMA) (copolymer), 61735-85-1.

References and Notes

(1) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(2) Skeist, I. *J. Am. Chem. Soc.* **1946**, *68*, 1781.
(3) Meyer, V. E.; Lowry, G. C. *J. Polym. Sci., Part A:* **1965**, *3*, 2843.
(4) Shawki, S. M.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1979**, *23*, 3155.
(5) Koike, Y.; Kimoto, Y.; Ohtsuka, Y. *J. Appl. Polym. Sci.* **1982**, *27*, 3253.
(6) Wall, F. T. *J. Am. Chem. Soc.* **1944**, *66*, 2050.
(7) Myagchenkov, V. A.; Frenkel', S. Ya. *Usp. Khim.* **1978**, *47*, 1261.
(8) Myagchenkov, V. A.; Frenkel', S. Ya. *Usp. Khim.* **1973**, *42*, 827.
(9) Nunes, R. W.; Huang, S. J.; Johnson, J. F. *Polym. Eng. Sci.* **1983**, *23*, 1.
(10) Johnson, M.; Karmo, T. S.; Smith, R. R. *Eur. Polym. J.* **1978**, *14*, 409.
(11) Dionisio, J. M.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 701.
(12) Teramachi, S.; Hasegawa, A.; Uchiyama, N. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *22*, 71.

(13) Teramachi, S.; Hasegawa, A.; Yoshida, S. *Macromolecules* **1983**, *16*, 542.
(14) O'Driscoll, K. F.; Kale, L. T.; Garcia Rubio, L. H.; Reilly, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2777.
(15) Inagaki, H.; Tanaka, T. In *Developments in Polymer Characterization*; Dawkins, J. V., Ed.; Applied Science: Barking, UK, 1982; Vol. 3, pp 1–32.
(16) Inagaki, H.; Matsuda, H.; Kamiyama, F. *Macromolecules* **1968**, *1*, 520.
(17) Kotaka, T.; White, J. L. *Macrmolecules* **1974**, *7*, 106.
(18) Ogawa, T.; Ishitobi, W. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 781.
(19) Teramachi, S.; Hasegawa, A.; Shima, Y.; Akatsuka, A.; Nakajima, M. *Macromolecules* **1972**, *12*, 992.
(20) Sato, H.; Takeuchi, H.; Suzuki, S.; Tanaka, Y. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 719.
(21) Ogawa, T.; Sakai, M. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1377.
(22) Teramachi, S.; Esaki, H. *Polym. J. (Tokyo)* **1975**, *7*, 593.
(23) Glöckner, G.; Koningsveld, R. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 529.
(24) Danielewicz, M.; Kubín, M. *J. Appl. Polym. Sci.* **1981**, *26*, 951.
(25) Danielewicz, M.; Kubín, M.; Vozka, S. *J. Appl. Polym. Sci.* **1982**, *27*, 3629.
(26) Stejskal, J.; Kratochvíl, P. *Macromolecules* **1978**, *11*, 1097.
(27) Arranz, F.; Sánchez-Chaves, M.; Molinero, A.; Martínez, R. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 297.
(28) Teramachi, S.; Kato, Y. *J. Macromol. Sci., Chem.* **1970**, *4*, 1785.
(29) Teramachi, S.; Kato, Y. *Macromolecules* **1971**, *4*, 54.
(30) Teramachi, S.; Fukao, T. *Polym. J. (Tokyo)* **1974**, *6*, 532.
(31) Bourguignon, J. J.; Bellissent, H.; Galin, J. C. *Polymer* **1977**, *18*, 937.
(32) Stejskal, J.; Kratochvíl, P.; Straková, D. *Macromolecules* **1981**, *14*, 150.
(33) Guyot, A.; Guillot, J. *J. Chim. Phys.* **1964**, *61*, 1434.
(34) Spinner, I. H.; Lu, B. C.-Y.; Graydon, W. F. *J. Am. Chem. Soc.* **1955**, *77*, 2198.
(35) Ring, W. *Makromol. Chem.* **1967**, *101*, 145.
(36) Myagchenkov, V. A.; Frenkel', S. Ya. *Vysokomol. Soedin., Ser. A* **1969**, *11*, 2348.
(37) Kruse, R. L. *J. Polym. Sci., Part B:* **1967**, *5*, 437.
(38) Stejskal, J.; Janča, J.; Kratochvíl, P. *Polym. J. (Tokyo)* **1976**, *6*, 549.
(39) Kratochvíl, P.; Straková, D.; Stejskal, J. *Polym. Commun.* **1985**, *26*, 202.
(40) Petrak, K. L.; Pitts, E. *Polymer* **1983**, *24*, 729.
(41) Stejskal, J.; Straková, D.; Procházka, O.; Kratochvíl, P. *Collect. Czech. Chem. Commun.* **1983**, *48*, 2656.
(42) Numerical values of data presented in figures are available on request.

Characterization of Poly(1,4-phenyleneterephthalamide) in Concentrated Sulfuric Acid. 4. Dilute and Semidilute Solution Regimes

Qicong Ying and Benjamin Chu*

Departments of Chemistry and Materials Science and Engineering, State University of New York at Stony Brook, Long Island, New York 11794-3400. *Received October 9, 1985*

ABSTRACT: From our analysis of the concentration and angular dependence of the static and dynamic properties (excess Rayleigh ratio ΔR_{vv}, radius of gyration R_g, hydrodynamic radius R_h, characteristic decay time Γ^{-1}, and second virial coefficients A_2 and k_d) of poly(1,4-phenyleneterephthalamide) (PPTA) in concentrated sulfuric acid (with and without the addition of a small amount of K_2SO_4), we have been able to examine the crossover behavior from the dilute to the semidilute solution regime for a rodlike polymer in solution. According to the scaling theory, the overlap concentration C^* for random coils is $\sim M/(N_A R_g^3)$, with M and N_A being the molecular weight and the Avogadro number, respectively. For rod macromolecules, $M/(N_A L^3) \lesssim C^*$. From semidilute to concentrated solution, an additional crossover behavior takes place. For rod macromolecules, $C^{**} \lesssim M/(N_A d L^2)$, with d and L being the rod diameter and length, respectively. In plots of $\lim_{K\to 0} [\Delta R_{vv}/(HC)]$ vs. concentration, the concentration C_m at which $\lim_{K\to 0} [\Delta R_{vv}/(HC)]$ shows a minimum can be represented by a modified Doi–Edwards inequality: $C_m \lesssim M/(N_A d^* L^{*2})$, with d^* and L^* being an effective diameter and an effective length of the macromolecule. K is the magnitude of the momentum transfer vector, ΔR is the excess Rayleigh ratio, and H is an optical constant. In a plot of $\log [M_{app}(HC/\Delta R_{vv}) - 1]$ vs. $\log (C/C_m)$, where M_{app} is the apparent molecular weight, the slope is equal to 1 for $C < C_m$ as de Gennes has predicted. The correlation length corresponding to the apparent root mean square radius of gyration at finite concentration was found to increase sharply above C_m, similar to the observation made by Burchard for aqueous poly(vinylpyrrolidone) solutions in the semidilute solution region.

I. Introduction

In previous papers,[1-3] we have characterized the dilute solution properties of poly(1,4-phenyleneterephthalamide) (PPTA) in concentrated sulfuric acid (with and without a small amount of K_2SO_4) using light scattering (LS) intensity and line-width measurements. We have been able to estimate the molecular weight dependences of intrinsic viscosity, of radius of gyration $\langle R_g \rangle_z^{1/2}$, and of translational diffusion coefficient $\bar{D}_z$ as well as the persistence length ρ ($\sim$290 Å) of PPTA in concentrated sulfuric acid. In addition, we have been able to estimate the molecular weight distributions of unfractionated PPTA samples[3] and to devise a simple calibration technique capable of monitoring molecular weight as well as molecular weight polydispersity index changes.[4] In this article, we present the crossover behavior for PPTA in concentrated sulfuric acid, with and without the addition of a small amount of K_2SO_4. Rodlike polymers are prone to interchain association.[5] Therefore, at higher solution concentrations interchain interactions may play an important role in the crossover behavior from the dilute to the semidilute solution regime. The behavior of the threshold concentration from dilute to semidilute solution is controlled by chain rigidity as well as molecular size. All experiments, including sample preparation and instrumentation, follow the same procedures as described in detail elsewhere.[2,3]

II. Dilute Solution Properties

Dynamic light scattering (LS) in combination with static light scattering intensity measurements has been shown to be a valuable approach to deduce information about macromolecular size, shape, molecular weight distribution,