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On the Cooccurrence of Demixing and Thermoreversible Gelation of Polymer Solutions. 3. Overall View

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ABSTRACT: The gelation of sufficiently concentrated solutions of poly(*n*-butyl methacrylate) (PBMA) in the vicinity of phase separation conditions is attributed to extraordinarily large enthalpies of mixing. These specific thermodynamic conditions render the opening of intersegmental contacts difficult and lead to a pronounced increase of viscometric relaxation times and eventually to gelation. On the basis of the experimentally determined value of −6 kJ for the heat of formation of 1 mol of intersegmental contacts out of 2 mol of solvent/segment contacts and −37 kJ, observed for the heat of gelation per mole of cross-links, one can estimate that a single cross-link may consist of approximately six segments. The characteristics of the thermodynamic mixing functions indicate that the molecular explanation for the cooccurrence of phase separation and thermoreversible gelation of the solutions of PBMA lies in the formation of locally highly ordered and energetically very favorable contacts between the *n*-butyl side groups of the monomeric units.

Introduction

Since the early report of Hardy[1] in 1899, thermoreversible gelation has been observed with both biological[2–4] and systhetic[5–14] polymers in solution. Two phenomena were always related to gelation: crystallization and phase separation.

In the explanation via crystallization, even in the case of polymers that normally do not crystallize in the pure state gelation is attributed[13,15] to the "copolymeric nature" of polymer molecules. A polymer may contain a few sequences of crystallizable segments, which upon crystallization form network junctions. The noncrystallizable parts of the chain are free from this ordering and just connect the crystallites, preventing the polymer from coming out of the solution, i.e., phase separating. The influence of tacticity in gelation by crystallization has been largely discussed.[5,6,16,17] It has also been stated[18] that crystallization may in many cases not be responsible for gelation itself but only contribute to gel stability by the formation of microcrystalline junction points.

The explanation of gelation via phase separation rests on numerous experimental observations concerning the cooccurrence of these two phenomena.[2,3,7,19,20] In the absence of especially favorable polymer/polymer interactions in a macromolecular solution, contacts between segments of different polymer chains lead to a statistically fluctuating network with very short-lived junctions.[3] When sufficiently favorable interactions exist, more stable network junctions are however formed and a macroscopic gel is observed. If the polymer solution phase separates prior to gelling, compact aggregates are often observed, which upon prolonged standing may lead to syneresis. Naturally gelation is not governed by the polymer characteristics alone but by the system as a whole, where specific solvent/polymer and polymer/polymer interactions expectedly play an important role.

In the present series of papers, the cooccurrence of gelation and phase separation is studied for solutions of poly(*n*-butyl methacrylate) (PBMA) in various Θ-solvents. In the first part,[21] experimental facts were collected; the second part[22] contains a comparison of Flory–Huggins parameters of gelling solutions to those of nongelling solutions. The current paper attempts to give a total view of the specific factors leading to the cooccurrence of phase separation and thermoreversible gelation with some polymer/solvent systems, while gelation is absent with most other demixing polymer solutions. In the context of this discussion, the integral thermodynamic quantities are needed rather than the partial ones of the solvent, reported in part 2;[22] for this reason, a further analysis of these data is first performed.

Additional Thermodynamic Evaluation

General Remarks. Due to the fact that the Flory–Huggins interaction parameters χ (determined from the activity of the solvent) were found to depend strongly on composition,[22] the differential interaction parameters are not identical with the integral ones.

By definition the following equations hold true:

$$g \equiv \frac{\Delta G^{\mathrm{R}}}{RTx_1\varphi_2} \tag{1}$$

$$\chi \equiv \frac{\Delta G_1^{\mathrm{R}}}{RT\varphi_2^2} \tag{2}$$

$$\xi \equiv \frac{\Delta G_2^{\mathrm{R}}}{RTN\varphi_1^2} \tag{3}$$

g is the integral interaction parameter, and χ and ξ are the partial interaction parameters determined by the activity of the solvent (index 1) and the polymer (index 2), respectively. φ_i are volume fractions, x_i are mole fractions, and N is the ratio or the molar volumes of polymer and solvent (proportional to the degree of polymerization). ΔG^{R} signifies the different residual molar Gibbs energies of mixing, which measure the deviation of a real from a purely combinatorial mixture, the latter being defined by

$$\Delta G^{\mathrm{comb}} = RT(x_1 \ln \varphi_1 + x_2 \ln \varphi_2) \tag{4}$$

From phenomenological thermodynamics one obtains the following interrelations between the different interaction parameters:[23]

$$g = \varphi_2\chi + (1 - \varphi_2)\xi \tag{5}$$

$$\chi = g - (1 - \varphi_2)\frac{\partial g}{\partial \varphi_2} \tag{6}$$

$$\xi = g + \varphi_2\frac{\partial g}{\partial \varphi_2} \tag{7}$$

If χ is given in terms of a series expansion

$$\chi = \sum_0^m \chi_i\varphi_2^{\,i} \tag{8}$$

Table I
Coefficients of the Series Expansion for the Concentration Dependence of the Integral Interaction Parameter *g* (Eq 1 and 9) for the Systems 2-Propanol/Poly(*n*-butyl methacrylate) and Ethanol/Poly(*n*-butyl methacrylate) at the Indicated Temperatures

	2-POH/PBMA				ETOH/PBMA		
T/K	g_0	g_1	g_2	T/K	g_0	g_1	g_2
300	0.7879	0.3064	0.2125	313	0.8240	0.3136	0.2452
314	0.7501	0.2985	0.1581	323	0.7892	0.3007	0.1967
329	0.7006	0.2717	0.1397	333	0.7643	0.2881	0.1385
344	0.6624	0.2610	0.1088	343	0.7366	0.2666	0.1006
359	0.6231	0.2338	0.1042	354	0.7116	0.2490	0.0529

the other two interaction parameters can be formulated analogously

$$g = \sum_0^m g_i \varphi_2^{\,i} \tag{9}$$

and

$$\xi = \sum_0^m \xi_i \varphi_2^{\,i} \tag{10}$$

where the individual coefficients of these series can be expressed in terms of the normally measured χ_i values in the following way:

$$g_i = \sum_i^m \frac{\chi_i}{i+1} \tag{11}$$

and

$$\xi_i = (i+1)\sum_i^m \frac{\chi_i}{i+1} \tag{12}$$

For most of the systems lacking specific interactions, like OH bonds, $m = 2$ suffices to describe the experimental findings.

If the experimentally determined χ values are represented by the closed expression[24]

$$\chi = \alpha + \frac{\beta(1-\gamma)}{(1-\gamma\varphi_2)^2} \tag{13}$$

the following relations result for g and ξ:

$$g = \alpha + \frac{\beta}{1-\gamma\varphi_2} \tag{14}$$

and

$$\xi = \alpha + \frac{\beta}{(1-\gamma\varphi_2)^2} \tag{15}$$

where α, β, and γ are constants for a given system at constant T and p.

In addition to the Gibbs energies (and the corresponding interaction parameters) themselves, their enthalpy and entropy parts are of special interest, since they give information on the depth of the potential well of neighboring particles. These contributions are (as formulated for g) accessible from the temperature dependences of the interaction parameters

$$g_H = -T\left(\frac{\partial g}{\partial T}\right) \tag{16}$$

and the Gibbs–Helmholtz equation, which in this particular case is given by eq 17

$$g = g_H + g_S = \frac{\Delta H}{RTx_1\varphi_2} - \frac{\Delta S^R}{Rx_1\varphi_2} \tag{17}$$

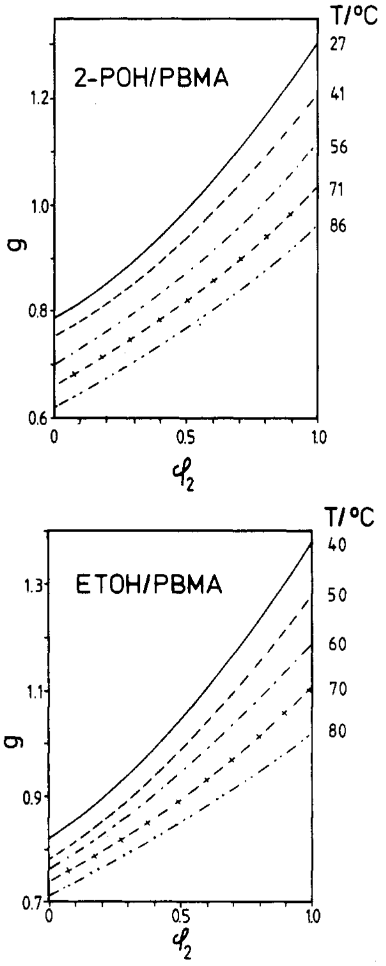

Figure 1. Integral interaction parameter g (eq 1) as a function of the volume fraction φ_2 of the polymer for the systems 2-propanol/poly(*n*-butyl methacrylate) (2-POH/PBMA) and ethanol/PBMA (ETOH/PBMA) for the indicated temperatures.

Table II
Constants of Eq 13–15, Giving the Concentration Dependence of the Different Interaction Parameters
$\beta = \beta_0 + (\beta_1/T)$

system	α	β_0	β_1/K	γ
CH/PS[a]	−0.1597	0.4987	111.74	0.2365
TBA/PS[b]	+0.1593w	0.5245w	29.678w	0.4575w

[a] The data are based on volume fractions as described in the text. [b] The data were obtained by consistently replacing volume fractions by weight fraction; they are marked with the index w.

Solutions of PBMA. Table I gives the experimentally determined[22] g_i values for the systems 2-propanol/PBMA and ethanol/PBMA. The corresponding dependence of g on concentration is graphically shown in Figure 1 for five temperatures. The variation of g_H and g_S, as obtained according to eq 16 and 17, can be seen from Figures 2 and 3; for comparison these graphs also contain the results for polystyrene.

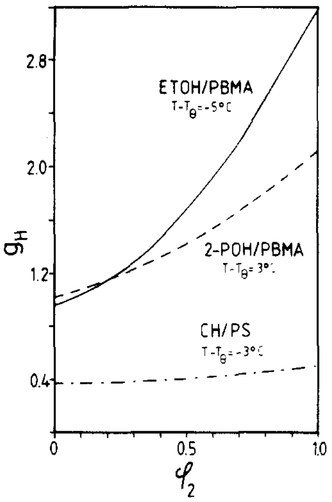

Figure 2. Enthalpic contributions g_H (eq 16 and 17) to the integral interaction parameters g as a function of the volume fraction φ_2 of polymer for the indicated systems and distances from the respective Θ-temperatures (CH/PS, cyclohexane/poly(styrene)).

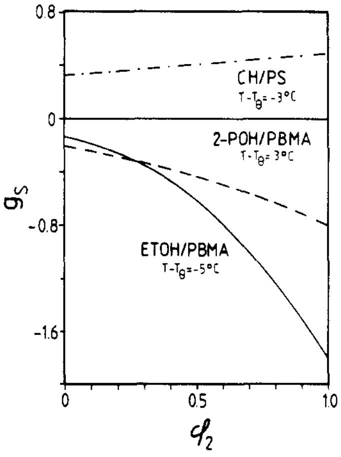

Figure 3. Entropic contributions g_S (eq 16 and 17) to the integral interaction parameter g as a function of the volume fraction φ_2 of polymer for the indicated systems and distances from the respective Θ-temperatures.

Solutions of Polystyrene. The thermodynamic data from these nongelling solutions were reported in terms of eq 13–15. In the case of cyclohexane they stem from critical demixing data;[24] in the case of *tert*-butyl acetate[25] additional vapor pressure and inverse gas chromatography measurements were performed. Table II collects the different characteristic parameters of the above equations. The concentration dependence of g looks very similar to that shown in Figure 1 for the solutions of PBMA; the enthalpy and entropy contributions to the integral interaction parameter, however, differ considerably as demonstrated in Figures 2 and 3.

Discussion

As already stated implicitly, two "pure bred" mechanisms of the thermoreversible gelation of polymer solutions can be distinguished: the formation of physical cross-links via highly ordered crystallites or via sufficiently stable, amorphous aggregates of polymer strands. In the following the arguments that can be obtained from the present results in favor of or against these two extreme cases are presented and supplemented by evidence from dynamic measurements.

Crystallites. The length of the n-alkyl group in a particular poly(n-alkyl methacrylate) governs the tendency of this material to crystallize and consequently influences the susceptibility of its solutions to thermoreversible gelation. Shibaev et al.[26-30] investigated gelation of comblike acrylic and methacrylic polymers with long ($n > 10$) side chains, showing (by X-ray investigations) that the phenomenon is accompanied by crystallization of these groups pending on the macromolecular backbone. The increase in the gelation temperature, observed upon a rise in the length of the side chain, was attributed to an intensification of dispersion interactions between these groups.

With the present solutions of PBMA, however, the occurrence of cross-links via true crystallites appears highly unlikely: The gels formed from them do not show birefringence when analyzed in the polarized microscope, and no characteristic crystallization band can be observed in DSC experiments. Furthermore, experiments with solutions of poly(n-decyl methacrylates) in Θ-solvents did not yield indications of a cooccurrence of phase separation and thermoreversible gelation,[31] characteristic of PBMA. Consequently, the explanation has to be sought in other peculiarities of the present solutions, above all in the characteristics of their thermodynamic behavior.

Gibbs Energies of Mixing. In order to determine the influence of the Gibbs energy of mixing on the ability of a polymer solution to gel, these quantities have been plotted as a function of concentration for various gel-forming and non-gel-forming systems. Figure 4 shows the experimentally determined ΔG, the corresponding combinatorial ΔG^{comb}, and the residual Gibbs energies of mixing ΔG^{R} (i.e., the difference between these two values) as functions of the volume fraction of the polymer for two solutions of PBMA (gel-forming) and two solutions of PS (non-gel-forming). These quantities refer to 1 *base* mole instead of 1 mol of mixture; here the extensive Gibbs energies of mixing have not been divided by $n_1 + n_2$, the sum

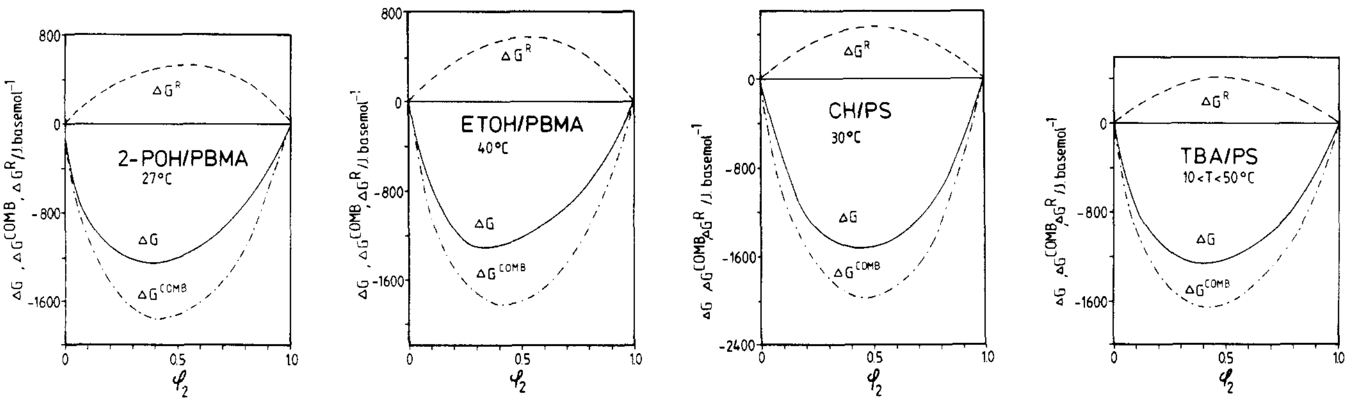

Figure 4. Base molar Gibbs energies of mixing: (—) experimental, (-·-): combinatorial (eq 4), (---): residual (experimental − combinatorial). Systems and temperatures are given in the graphs. TBA indicates *tert*-butyl acetate.

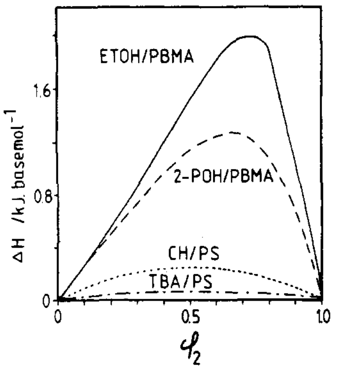

Figure 5. Base molar enthalpy of mixing as a function of the volume fraction of polymer; the data refer to the following temperature intervals: ETOH/PMBA, 40–81 °C; 2-POH/PBMA, 27–86 °C; CH/PS, 30–70 °C; TBA/PS, 10–50 °C.

of the moles of solvent and solute, but by $n_1 + Pn_2$, where P is the degree of polymerization.

Comparing the maxima of ΔG^R, one observes the following order of increasing mixing tendency: ETOH/PBMA (580 kJ/mol), 2-POH/PBMA (520 kJ/mol), CH/PS (460 kJ/mol), and TBA/PS (400 kJ/mol). In the following section it is determined whether the lower tendency of PBMA to form homogeneous solutions as compared with that of PS (i.e., the higher number of contacting segments contributing to the development of a network in the former case) already suffices to explain why the solutions of this polymer gel, in contrast to those of PS.

If the formation of contacts between solvent molecules (1) and polymer segments (S) is treated (in complete analogy to the procedure of Tompa[32]) as if it were a chemical equilibrium, symbolically written as

$$(11) + (SS) = 2(1S) \tag{18}$$

then the actual number of intersegmental contacts X_{SS} can be related to X_{SS}^{comb}, the purely combinatorial one, by

$$X_{SS} = X_{SS}^{comb}\left(\frac{1 - K(1 - \varphi_2)}{\varphi_2}\right) \tag{19}$$

where

$$X_{SS}^{comb} = (\text{prop})\varphi_2^2 \tag{20}$$

and K is given by the quadratic equation 21 containing the experimentally determined interaction parameter g

$$\varphi_1\varphi_2(e^{2g} - 1)K^2 + K - 1 = 0 \tag{21}$$

For very poor thermodynamic conditions close to phase separation (large g, cf. Figure 1), the above relations indeed yield considerably higher values for X_{SS}, the number of intersegmental contacts, than calculated combinatorically. At $\varphi_2 = 0.15$ and the temperatures given in Figure 4, for instance, X_{SS} is approximately twice X_{SS}^{comb} for PBMA, but even with PS it is already 80–90% higher than purely statistical. This finding that both systems yield comparably high X_{SS} values but that only one forms a gel leads to the conclusion that an explanation on the basis of the Gibbs energy of mixing (although it acts in the right direction) is insufficient.

Enthalpy and Residual Entropy of Mixing. The stability of intersegmental contacts with respect to thermal motion is primarily determined by the energy required to open such a contact, which in turn is measured by the enthalpy of mixing. Figure 5 shows these data for the four systems of interest.

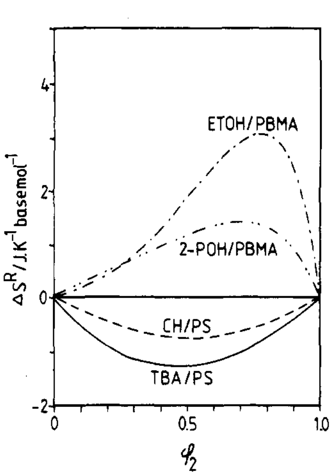

Figure 6. Base molar residual entropy of mixing as a function of the volume fraction of the polymer; the data refer to the same T intervals as in Figure 5.

The almost 1 order of magnitude larger enthalpies of mixing of PBMA plus Θ-solvent, as compared to those of PS, stabilize the intersegmental contacts. Excluding cooperative effects as well as changes in the preexponential factor and taking the g_H values as the exponents of the Boltzmann factors in the rate equations for the separation of two polymer segments already lead to an increase in the average lifetime of an intersegmental contact of PBMA over that of PS by a factor of approximately 3.

The residual entropies of mixing depicted in Figure 6 should also reflect the energetically very favorable interactions between the side groups of PBMA, which lead to large numbers of intersegmental contacts in the gelling solutions. Indeed, positive ΔS^R values are observed with PBMA, as compared with the normal behavior (negative values) of PS.

All findings concerning ΔH and ΔS^R can be rationalized by postulating that (i) the interactions between the side groups of PBMA are energetically very favorable and lead to a comparatively high degree of ordering in the pure polymer and (ii) the pure solvent is also to some extent ordered via the OH bonds of the alcohols: in such a case the energetically extremely unfavorable rupture of contacts between like components (large ΔH values) is only possible because of the great extent of disordering associated therewith (large ΔS^R values). In other words, the particularities of enthalpy and entropy cancel to a great extent, so that the Gibbs energies of mixing remain comparable for chemically very unlike polymer/solvent systems, despite the pronounced differences in its thermodynamic constituents.

Molecular Mobility. The energetic situation just discussed should influence not only the thermal stability of junction points but also the flow behavior of the present solutions, since it can be anticipated that the liquids become more viscous as the stability of the physical cross-links increases. Furthermore, the average lifetime of such physical junction points should be reflected in the non-Newtonian behavior of these solutions.

Indeed it has been observed (by comparing the zero-shear viscosity of solutions of PBMA with that of poly(methyl methacrylate) (PMMA) and poly(n-decyl methacrylate) (PDMA) in the corresponding Θ-solvents at approximately the same coil-overlap concentrations[31,33]) that PBMA assumes a prominent place within this series of poly(n-alkyl methacrylates) by showing the highest viscosity under comparable conditions (Figure 7). The same statement holds true for τ_0, the characteristic viscometric relaxation time (Figure 8). Again PBMA exhibits note-

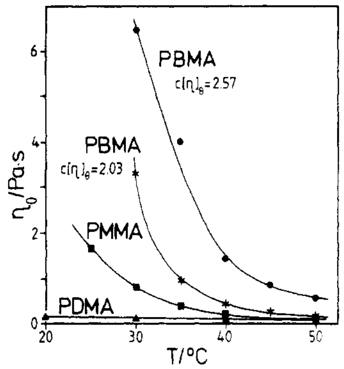

Figure 7. Temperature dependence of the zero-shear viscosity η_0 for solutions of different poly(n-alkyl methacrylates) in Θ-solvents.[31,33] The coil-overlap parameters (dimensionless product of intrinsic viscosity and polymer concentration) are given in parenthesis for Θ-conditions: heptanone-3/poly(methyl methacrylate) (2.39); 2-POH/PBMA (2.03 and 2.57); 1-pentanol/poly(n-decyl methacrylate) (3.41).

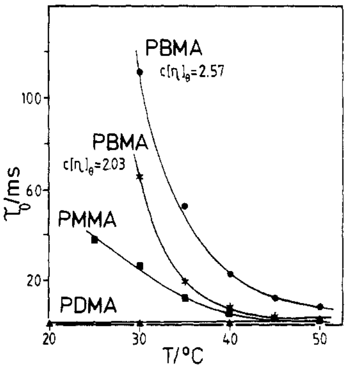

Figure 8. Temperature dependence of the characteristic viscometric relaxation times[31,33] (approximately equal to the inverse of the shear-rate where shear-thinning sets in) for the same systems and conditions as in Figure 7.

worthy behavior with its manyfold slower disentanglement processes which reflect the energetic difficulties in opening its intersegmental contacts.

Conclusions

All the results presented for the thermoreversible gelation of the solutions of PBMA when they are close to their demixing clearly favor the concept of physical cross-links via amorphous aggregates; the formation of network points via larger crystallites can be practically ruled out by the absence of birefringence and of melting peaks in DSC experiments.

The question arises, however, whether a clear distinction between the above gelation mechanisms can in reality be made: Even macroscopically amorphous aggregates are likely to be ordered on a smaller scale (so it has to be anticipated from molecular models that the n-butyl groups of different polymer strands intercalate) and crystallites tend to become rather imperfect upon the reduction of their size (due the increase in the surface/volume ratio). The only two requirements that have to be met for a thermoreversible solidification are a sufficiently large number of intersegmental contacts between the individual polymer molecules plus a large enough average lifetime of these temporary cross-links.

The requirement concerning the contact statistics is obviously always fulfilled for sufficiently concentrated polymer solutions in thermodynamically poor solvents. The reason for the observation that phase separation is associated with thermoreversible gelation only sometimes, but not always, lies obviously in different average lifetimes of these cross-linking loci. The stability of physical contacts between polymer segments with respect to thermal motion is primarily determined by the ratio of the molar energy required to open such a contact, inserting solvent molecules, and the thermal energy RT. In the case of cross-linking via amorphous aggregates, the above ratio is identical with g_H; values of less than 0.5 are observed for nongelling systems, as compared with values of up to more than 3 for gelling, as could be seen from Figure 2. In the case of crystallites their base molar heat of fusion divided by RT has to be added to g_H; this extra stabilization leads to the conclusion that crystallizable polymers should exhibit the cooccurrence of phase separation and thermoreversible gelation even with only moderately endothermal solutions.

Following Eldridge and Ferry,[4] enthalpy considerations can also be used for some speculations concerning the number of segments participating in a physical cross-link. The comparison of the heat of gelation (−37 kJ/(mol of cross-links), cf. Figure 8, part 1) with the enthalpy of formation of 1 mol of intersegmental contacts from 2 mol of solvent–segment contacts ($-2g_HRT$ ca. 6 kJ/(base mol)) leads to ca. six segments per cross-link. This value is somewhat less than that reported[4] for gelatine gels (10–45), where hydrogen bonds (ca. 20 kJ/mol) were assumed responsible for network formation. On the basis of these data it has to be expected that the gels formed from solutions of PBMA are comparatively unstable against shear; there are indeed experimental indications for that (cf. part I).

Finally one could ask for the specific molecular requirements leading to particularly large enthalpies of mixing in combination with a still sufficiently high mixing tendency (i.e., the occurrence of an upper critical solution temperature and the cooccurrence of gelation). On the polymer side, the answer lies probably in a proper amphiphilic nature of the monomeric unit plus a suitable molecular architecture that allows energetically very favorable interactions via local ordering. This conclusion is based on the observation that neither too short n-alkyl branches of poly(n-alkyl methacrylates) (like methyl) nor too long ones (like decyl) lead to the cooccurrence of phase separation and gelation but only a well balanced length like butyl. On the solvent side, the requirements seem to be much less stringent, as long as Θ-conditions can be realized at low enough temperatures; this is demonstrated by the fact that no principle differences are observed whether either alcohols or hydrocarbons are used as Θ-solvents for PBMA.

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Registry No. PBMA, 9003-63-8; $H_3CCH(OH)CH_3$, 67-63-0; H_3CCH_2OH, 64-17-5.

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Depolarization Ratios and Rigidity of Aromatic Polyamides

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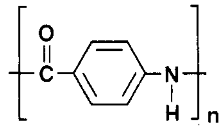
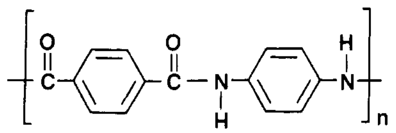
ABSTRACT: Monodisperse oligomers and several unfractionated polymers of poly(*p*-benzanilide–terephthalamide) (*p*-BT) were prepared and characterized. Their depolarization ratios were measured in concentrated (96%) sulfuric acid and they produced optical anisotropy values essentially the same as those of poly(*p*-phenylene terephthalamide) (*p*-PT) of comparable M_w. A numerical fit to our *p*-BT data and literature data for fractionated *p*-PT yielded a persistance length of 113 Å. The unfractionated *p*-PT, particularly at high molecular weights, tended to yield higher depolarization ratios and, consequently, higher persistance lengths than equivalent fractionated material, possibly due to high polydispersity.

Introduction

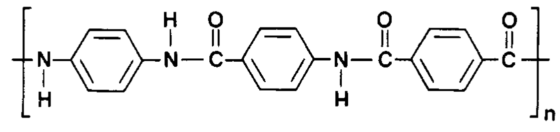
Due to the remarkable tensile properties and thermal stability of their fibers, there is a great deal of practical and theoretical interest in the properties of para-substituted aromatic polyamides, particularily poly(*p*-benzamide) (*p*-BA) and poly(*p*-phenylene terephthalamide) (*p*-PT). Recently, one of us has studied[1] the behavior of monodisperse oligomers and higher molecular weight homologues of the polymer poly(*p*-benzanilide–terephthalamide) (*p*-BT), which can be considered to be a 1:1 copolymer of *p*-BA and *p*-PT.



poly (p-benzamide) (p-BA)



poly (1,4-phenylene terephthalamide) (p-PT)



poly (p-benzanilide terephthalamide) (p-BT)

The properties of *p*-BA and *p*-PT in dilute solution have not been extensively measured, chiefly because of the following: (a) in *N,N*-dimethylacetamide (DMAc)/LiCl solvent mixtures, the aromatic polyamides show strong effects of molecular aggregation; (b) other useful solvents, such as concentrated sulfuric acid or chlorosulfonic acid, are highly corrosive and possess high viscosity; (c) a protracted exposure to these strong acids results not only in a slow degradation of the aromatic polyamides but also in the sulfonation of their aromatic rings.

The existing measurements have indicated that the above aromatic polyamides are very rigid, as one would expect. From intrinsic viscosity ([η]) and molecular weight (M_w) measurements, the Mark–Houwink exponent (a) in

$$[\eta] = K[\mathrm{M}]^a \qquad (1)$$

falls in the interval $1.0 < a \leq 1.85$, with the most common values obtained being around 1.1–1.2. Because they are higher than the theoretically expected values ($a = 1.7$) for monodisperse completely rigid rodlike molecules of comparable lengths,[1-3] values of, say, $a = 1.85$[4] appear to reflect the strong aggregation effect of *p*-BA in DMAc/3% LiCl and not the true behavior of individually disperse *p*-BA macromolecules.

Furthermore, persistence lengths (q) from viscosity, depolarization ratio, radius of gyration, electric birefringence, and flow birefringence measurements cover a huge range of values. Even when measured only in concentrated (96%) sulfuric acid, where aggregation effects are presumably eliminated, one gleans from the literature values of $325 \leq q \leq 1050$ Å for *p*-BA and $150 \leq q \leq 650$ Å for *p*-PT.[5-16] The q values are tabulated in Table I. Diffusion and sedimentation experiments appear not to be suffi-

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