Thermoreversible Gelation and Vitrification of Highly Concentrated Polymer Solutions under Poor Thermodynamic Conditions

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ABSTRACT: Differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy (DRS) demonstrate that highly concentrated solutions of poly(*n*-butyl methacrylate) (PBMA; $M_w = 450\,000$, $M_w/M_n = 1.06$) in 2-propanol (2-POH) solidify upon cooling in two clearly distinguishable steps. With this endothermal system, for which the Θ temperature (24 °C) is almost identical with the glass transition temperature of the pure polymer (22 °C), the solutions gel thermoreversibly some 60–40 °C before they become glassy. The gelation is interpreted in terms of noncrystalline physical cross-links, which result from the preference of the energetically highly favored polymer/polymer contacts over polymer/solvent contacts; the resulting intersegmental clusters amplify a partial freezing-in of the mobility of the macromolecules that can already be observed in the absence of solvent by means of DRS measurements. Qualitatively the glass transition temperature of the pure PBMA is changed by the addition of 2-POH in the usual way. The low solvent quality, however, causes extra effects, which favor the vitrification. A so far only empirical equation is proposed to describe these thermodynamic contributions.

Introduction

In liquid mixtures, the molecular mobility of the components is influenced by the thermodynamic interaction between them. For many systems the effects remain moderate, but sometimes they can become very pronounced. An outstanding example of the latter case is the frequently observed co-occurrence of phase separation and thermoreversible gelation.[1-10]

For moderately concentrated solutions of poly(*n*-butyl methacrylate) (PBMA) in isopropyl alcohol (2-POH), the gelation in the vicinity of phase-separation conditions could be attributed to extraordinarily large enthalpies of mixing,[9] which lead to temporary, but long-lived, cross-links. This particular situation also expresses itself in a pronounced increase of the characteristic viscometric relaxation times of the polymer as the temperature[11] or the pressure[12] are varied such that the solvent deteriorates.

One interesting observation with moderately concentrated solutions of PBMA in 2-POH concerns the fact that some of them gel at temperatures that are higher than the glass transition temperature of the pure polymer. At least two explanations appear feasible: Assuming that gelation and glassy solidification coincide, as reported[10] for solutions of atactic polystyrene, would imply the occurrence of extrema in the concentration dependence of that single transition temperature (caused by the particular thermodynamic situation). The other possible rationalization rests on the assumption that gelation and glassy solidification constitute two separate processes, i.e., that the system loses its fluidity in two steps.

The present study with highly concentrated solutions of PBMA in 2-POH was performed to decide between the above two cases and to learn more about the behavior of the polymer in that concentration and temperature regime. The term gelation is used even for very high polymer concentrations since this phenomenon does not change in principle as the composition is increased. Differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy (DRS) were chosen as methods to deal with the present question. Furthermore, NMR and rheological measurements are currently being made in order to obtain additional information on the relaxation of different parts of the macromolecule.

Experimental Section

Materials. Isopropyl alcohol p.a. (>99.7% GC) from Merck, Darmstadt, dried over a molecular sieve (3 Å) to remove the rest of the water was used as the solvent without further purification. The polymer samples were prepared by anionic polymerization by Röhm GmbH Darmstadt and fractionated to remove a high molecular weight tail in a methanol/acetone mixed solvent containing 52.4 vol % methanol. Poly(*n*-butyl methacrylate) (PBMA 520) has a molecular weight of $M_w = 450\,000$, and its molecular polydispersity $U = (M_w/M_n) - 1$ is 0.06. According to ^{13}C NMR measurements the polymer contains about 60% syndiotactic and 4% isotactic triads.

Preparation of the Samples. Samples for calorimetric measurements (DSC): Highly concentrated solutions of PBMA 520 in isopropyl alcohol were prepared by casting films from ca. 20 wt % solution of PBMA 520 in acetone (p.a.) and drying them under vacuum at 80 °C to constant weight. Comparison between DSC measurements made with solution-cast films and merely pressed polymer showed no significant differences in the results.

The carefully dried films were placed in a chamber with isopropyl alcohol and loaded via gas phase with solvent at temperatures higher than the Θ temperature (24.1 °C). Afterward, the solutions were left to homogenize for several days at 50–60 °C.

Samples for dielectric measurements: The solutions studied by dielectric relaxation spectroscopy (DRS) were prepared by analogy to the procedure described for the DSC measurements, except for the fact that freshly distilled THF was used instead of acetone, and the concentration of polymer was decreased to 10 wt % of polymer. The films were cast directly at the surface of the electrode (diameter 20 mm), since it turned out that smoother and more regular films of pure PBMA are obtained in this way. Quartz spacers of 46 μm thickness were placed on the surface of the lower electrode before casting, and these films

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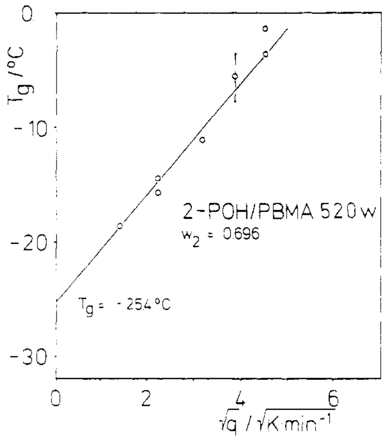

Figure 1. Example for the extrapolation of the glass transition temperature T_g obtained for the system 2-propanol/poly(*n*-butyl methacrylate) (M_w = 451 000) from DSC measurements to zero heating rate q; w_2, the weight fraction of the polymer, is indicated.

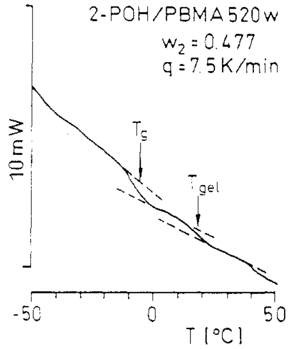

Figure 2. DSC heating diagram for a solution of 47.7 wt % of PBMA 520 in 2-POH, which was tempered 20 °C above T_g for 3 days to 1 week before cooling to -80 °C and heating with a rate of 7.5 K/min.

were dried under vacuum at elevated temperatures (80 °C) to weight constancy. The dried films were then loaded with isopropyl alcohol (as described in the section dealing with the calorimetric measurements) and kept at room temperature for 3–4 days in order to enable gelation. The upper electrode was mounted on top of the film supported by the lower one, and this assembly was put into a customary Teflon cell, which was sealed by O-rings in order to prevent leakage of the solvent.

Calorimetric Measurements. Glass transition temperatures T_g: The differential scanning calorimetry (DSC) measurements were carried out with a liquid-nitrogen-cooled DSC 30 apparatus from Mettler GmbH, Giessen, coupled with a digital data analysis system. Samples of 40–100 mg were filled into special DSC pans, which are hermetically lockable to withstand internal pressures up to 20 bar, and showed no measurable loss of weight over a period of months. To detect the glass transition temperature, T_g, of the solutions, DSC heating scans starting at -80 °C were recorded for different heating rates, q. The plots were evaluated by the midpoint method and the results extrapolated according to the equation[13]

$$T_g(q) = T_g(0) + a(q^{1/2}) \tag{1}$$

An example for this evaluation is shown in Figure 1. With the present system, only heating experiments are meaningful, since tempering the samples at temperatures higher than the boiling point leads to concentration shifts via evaporation, and condensation of the solvent during cooling effaces always the glass transition step.

Gelation temperatures T_{gel}: DSC scans performed with freshly prepared concentrated solutions of PBMA in isopropyl alcohol do not indicate a gel melting process. However, a second, weak step in the DSC curve above T_g can be observed, as shown in Figure 2, if the samples are treated in the following way: After tempering at a temperature ca. 20 °C higher than T_g but lower than T_{gel} for 2–3 days, they are cooled rapidly down to -80 °C and then reheated with a rate of 7.5 K/min. For increasing contents of polymer, the gelation steps broaden considerably. Nevertheless, T_{gel} data were determined, since it turned out that they are located on a curve that can be smoothly connected with the $T_{gel}(w_2)$ curve obtained for lower polymer concentration by viscometric means.[9]

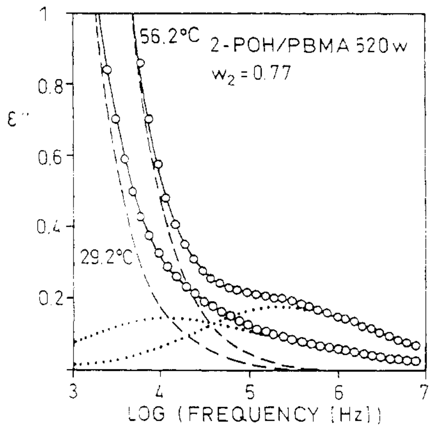

Figure 3. Example of the fitting procedure used in the evaluation of the dielectric loss data for a solution of 77 wt % of PBMA in 2-POH and the two indicated temperatures. The solid line connecting the measuring points is the sum of the fitting results for ϵ_r'' (···) and for ϵ_c'' (- - -).

For the evaluation of the DSC scans one has to decide whether the gelation should be treated as a first-order process (peak) or as a second-order process (step). Unfortunately, the magnitude of the heat effects and the precision of the measurements do not allow a clear distinction. Two observations are in favor of a treatment according to a second-order process: (i) the fact that neither the polymer solutions nor the pure solute crystallize, i.e., that no melting process should be associated with gelation, and (ii) that the midpoint of the second DSC step, taken as T_{gel}, agrees better with the viscometrically obtained gel curve, extrapolated into the region of high polymer concentration, than with the result of the other evaluation.

Dielectric Measurements (DRS). The frequency-dependent dielectric loss, $\epsilon''(\omega)$, was measured at constant temperature between 10 and 10^7 Hz using an ac bridge (HP 4192 A). Additional investigations on the pure PBMA sample have been carried out between 10^{-2} and 10^4 Hz, using a frequency response analyzer (Solartron Schlumberger 1254) combined with a special interface (Chelsea Dielectrics) for impedance matching, and between 10^6 and 10^9 Hz, using a high-frequency impedance analyzer (HP 4191 A). The temperature of the sample could be adjusted within 0.1 °C by a custom-made control system. A complete description of the experimental setup is given in ref 14. For the evaluation of the loss curves the well-known Havriliak–Negami formula has been used for the part ϵ_r^* of the complex dielectric function that is due to relaxational movements of the dipoles:[15]

$$\epsilon_r^*(\omega) = \epsilon_\infty + (\epsilon_{st} - \epsilon_\infty)/(1 + (i\omega\tau)^\alpha)^\beta \tag{2}$$

Here ϵ_{st} and ϵ_∞ represent the limits of the real part $\epsilon'(\omega)$ for $\omega \ll 1/\tau$ and $\omega \gg 1/\tau$, respectively; α and β are purely empirical parameters with values between 0 and 1. Debye behavior is obtained for $\alpha = \beta = 1$, while smaller α values account for a symmetrical and smaller β values for an asymmetrical broadening of the loss curve. The average relaxation time of the dipoles is characterized by the parameter τ. If log τ is plotted against the inverse temperature, the slope of the curve gives the apparent activation energy E^* of the relaxation process. Since pure isopropyl alcohol has a considerable dc conductivity (3.5 × 10^{-6} S/cm at 25 °C), there is an additional contribution $\epsilon_c''(\omega)$ to the dielectric loss, which in some cases exceeds ϵ_r'' by orders of magnitudes at low frequencies. It can be fitted well by the expression[16] $\epsilon_c''(\omega) = \sigma_0/(\epsilon_0\omega^p)$, where σ_0 is a frequency-independent conductivity, ϵ_0 is the dielectric constant in vacuo, and p is a parameter with a value close to 1. The total loss is the sum of the relaxational and conductivity contributions: $\epsilon'' = \epsilon_r'' + \epsilon_c''$. Figure 3 shows two representative curves with fitting results, where dotted lines denote ϵ_r'' and broken lines represent ϵ_c''.

Results

DSC Measurements. Glass transition temperatures: Vitrification data obtained from the calorimetric measurements are shown in Figure 4. This diagram reveals two basically different parts in the plots of T_g values extrapolated to zero heating rates versus polymer concentration. For the highest polymer concentrations ($0.8 < w_2 < 1$, with w_2 being the weight fraction of polymer) T_g decreases with an increasing amount of added solvent in the normal way. As soon as the glass transition curve crosses the demixing curve, however, T_g becomes independent of polymer concentration.

A feasible explanation for this behavior is provided by the hypothesis that the DSC diagram only monitors the vitrification of the polymer-enriched coexisting phase: If a sufficiently small amount of solvent is added to the pure polymer, it can be taken up quantitatively and the mixture remains homogeneous down to temperatures well below the glass transition of PBMA. When such a solution is cooled, it vitrifies in the usual manner and remains one phase at $T < T_g$. On the other hand, if the amount of the solvent added becomes too high, the polymer concentration of the solution under investigation falls below a certain critical value and the system will phase separate upon cooling prior to solidification; upon a continued reduction of T, the polymer-rich coexisting phase will become more concentrated until it finally reaches the composition w_2^*, at which the glass transition curve and the supercritical branch of the coexistence curves intersect (cf. Figure 4); under that condition this phase will vitrify. Since a polymer with a narrow molecular weight distribution was used, w_2^* does not depend on the initial concentration w_2^0 of the polymer, and this means that the solidification (as seen by the DSC) becomes independent of this variable. Such a behavior has also been found for other polymer–solvent systems exhibiting a miscibility gap.[10]

In many cases the concentration dependence of the glass transition curve can with good precision be approximated by the relation[17]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (3)$$

T_g means the glass transition temperature of the solution, T_{gi}s are the glass transition temperatures and w_is the weight fractions of the components, where the index 1 stands for the solvent and 2 for the polymer. The dependence $T_g(w_2)$ calculated from eq 3, shown in Figure 4 together with the experimental results, demonstrates that the measured T_g values are always larger than predicted by this equation.

Gelation temperatures: In Figure 5 the gelation temperatures obtained from DSC are plotted against the polymer concentration of the solutions. The heating rate was chosen to be 7.5 K/min in all cases. Extrapolating the T_{gel} data to zero heating rate according to eq 1 turned out to be impossible: at the higher q values the steps become blurred out, and at lower q values the signal to noise ratio is too small. In order to demonstrate the effects of the heating rate on T_g, the data for the same q value as applied in the determination of T_{gel} and the extrapolated results are also given in this graph. After melting the gels for the first time, it takes days to reestablish them within the DSC pans such that they can again be detected by this method.

DRS Measurements. Pure PBMA: Results published by other authors[18,19] suggest an interpretation of the main observable relaxation above T_g as a "mixed $\alpha\beta$-process". This term describes the strong coupling of the α relaxation (dynamic glass transition) and the local β relaxation (side-group motions).

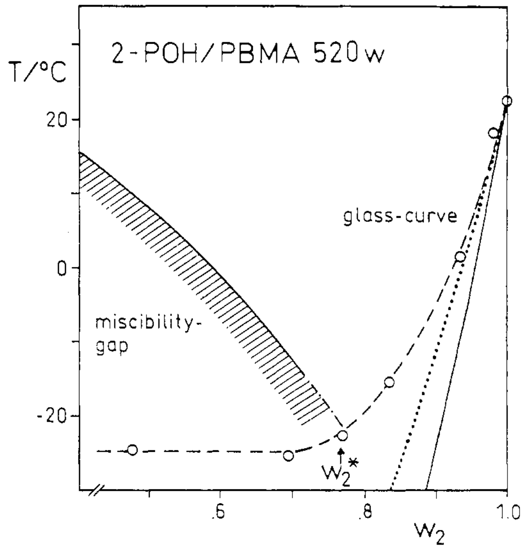

Figure 4. Concentration dependence of the glass transition temperature, T_g. Broken line: measured by DSC. Solid line: predicted from eq 3 with a T_{g1} value[28] of 104 K for 2-POH. Dotted line: calculated from eq 3 assuming that $T_{g1} = {}^2/_3$ of the melting temperature of 2-POH. The hatched area indicates the miscibility gap.

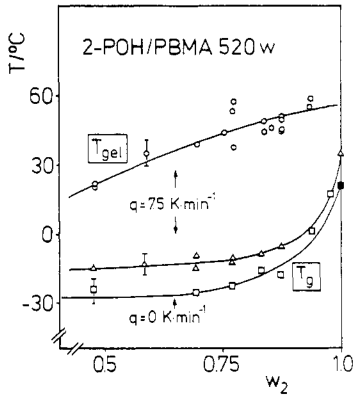

Figure 5. Concentration dependence of the gelation temperatures T_{gel} and of the glass transition temperatures T_g as determined by DSC for a constant heating rate q of 7.5 K/min; for the glass transition it is also demonstrated how the extrapolation to $q = 0$ changes the values.

Upon cooling, the maximum of the loss curve for the $\alpha\beta$-process starts to split up into the α- and β-curve in our measurements some 50 °C above T_g; under these conditions they are, however, hardly separable by a double Havriliak–Negami fit, since the processes occur near the lower limit of the experimentally accessible frequency range.

Figure 6 shows the activation diagram of *pure* PBMA, where the α, β, and $\alpha\beta$ relaxations are indicated by different symbols. For $T > T_g + 50$ °C a straight line is obtained, which corresponds to an Arrhenius-like $\alpha\beta$ process with a constant activation energy of $E^* = 35$ kJ/mol. Dynamic light scattering of PBMA by the method of photon correlation spectroscopy revealed a similar behavior for the characteristic relaxation times: for higher temperatures an Arrhenius-like process with $E^* = 35$ kJ/mol is observed, while—on approaching T_g—the curve splits up into two branches.[19]

Solutions of PBMA: These measurements were performed in 2-POH, starting at temperatures above T_g, but

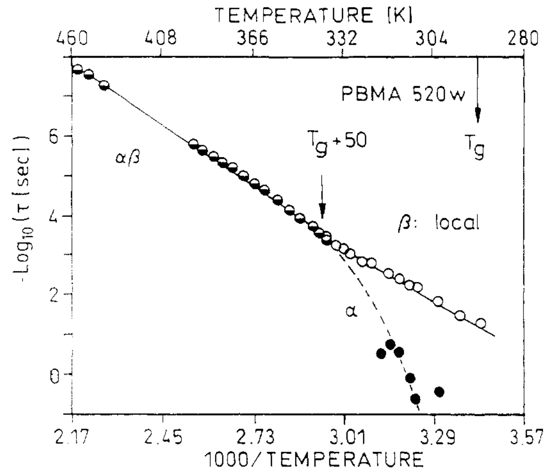

Figure 6. Activation diagram for the dielectric loss (negative logarithm of the average relaxation time τ of the dipoles versus T^{-1}) for pure PBMA 520. Half-filled symbols: $\alpha\beta$-process. Full symbols: α-process. Open symbols: β-process.

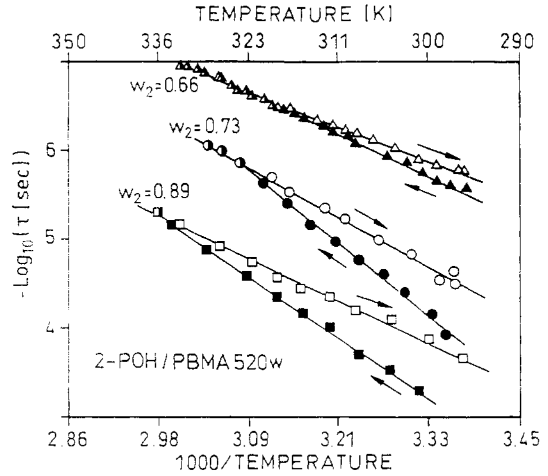

Figure 7. Activation polots of the system 2-POH/PBMA 520 for the indicated representative values of w_2. Full symbols: first heating. Open symbols: subsequent cooling.

well below T_{gel}, down to 60 wt % of the polymer; for still lower polymer concentrations, ϵ_r'' is completely concealed by ϵ_c'' due to the conductivity of the solvent and no separation of the two parts of ϵ'' is possible. As is shown in Figure 7, two significant differences in the activation diagrams with respect to the pure polymer are observed:

(a) With increasing concentration of the solvent, the curves are shifted to higher frequencies. This is due to the higher mobility of the dipoles in the gel (and also in the ungelled solution) as compared to pure PBMA. As a result of the experimental procedure, the numbers given in Figure 7 for the polymer concentrations are subject to considerable error. Estimates of the maximum loss of solvent during the introduction of the films into the measuring cell and assessment of reproducibilities lead to actual w_2 values, which can exceed the original weight-in concentration up to 5 wt %.

(b) Upon heating the gel for the first time, there is a transition of the straight line in the activation plot from one slope to another at some characteristic temperature (depending on w_2). The temperature at which the two straight lines intersect (Figure 8) is taken to be T_{gel}. It must be emphasized that, due to the small changes in the slopes, T_{gel} can only be determined with limited accuracy by means of DRS measurements.

If one repeats the measurements after waiting for several hours at the highest temperature (in the absence of the electrical field), no change in the slope of the activation plot can be observed, neither upon cooling nor upon heating. This situation remains unaltered even after waiting at the lowest temperature for several days. On the other hand, the regelation, as determined calorimetrically, is completed after that period. This difference between DRS and DSC might be caused by surface effects, which cannot be excluded in view of the low capacitor thickness of 46 μm. A detailed comparison of the differences observed with the two methods requires additional experiments.

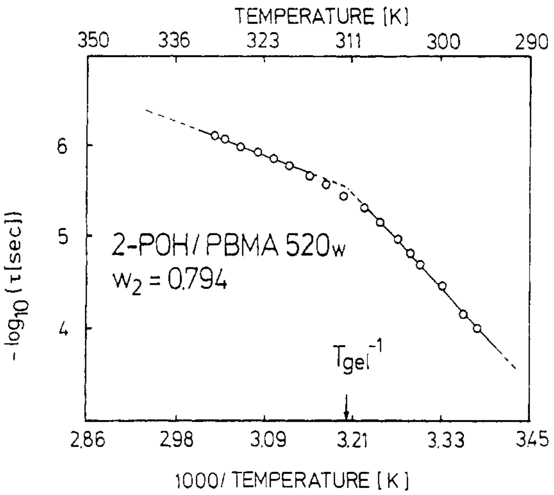

Figure 8. Activation plot for a 79.4 wt % solution of PBMA 520 in 2-POH and first heating; the intersect of their two linear parts is taken as the gelation temperature, T_{gel}.

Discussion

In the introduction the question was raised as to whether the gelation and the glassy solidification of highly concentrated solutions of PBMA in 2-POH coincide. On the basis of the results presented in the preceding section, an unequivocal answer can be given: The present system loses its fluidity upon cooling in two clearly separable steps, like the solutions of other polymers in thermodynamically bad solvents.[5-7]

Gelation temperatures: T_{gel} values determined by means of viscometric, DSC, or DRS experiments are identical within experimental error and their concentration dependence obeys, as demonstrated by Figure 9, the following equation[20]

$$\ln \varphi_2 = C + \Delta H_x/(RT_{gel}) \tag{4}$$

in which ΔH_x represents the heat associated with the addition of 1 mol of potential network junction points to the already formed network junctions and C is a constant.

In view of the experimental uncertainties, which are particularly large for high polymer contents where the measuring effects become vanishingly small, a straight line is drawn in Figure 9 despite the fact that the data points suggest a slight curvature. From the intercept of that line with the abscissa one can read that the T_{gel} value extrapolated for the pure polymer amounts to 53 °C, i.e., lies well above its glass transition of 22 °C.

The above results imply that there is no or only a small change in the gelation mechanism as the concentration increases and that the thermodynamic interpretation given for moderately concentrated solutions[9] remains valid. This in turn means that even with highly concentrated solutions of PBMA in 2-POH the energetically extremely favored contacts between the n-butyl side chains of the polymer over their contacts with the solvent yield cross-linking

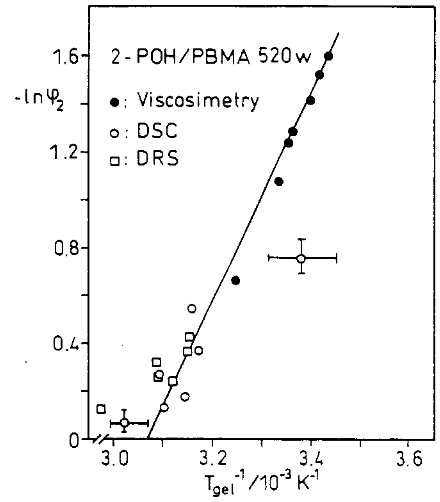

Figure 9. Ferry–Eldridge plot for the system 2-POH/PBMA 520. Correlation between the inverse of the gelation temperatures T_{gel} (determined by means of the different methods indicated in the graph) and $-\ln \varphi_2$, where φ_2 is the volume fraction of the polymer; the viscometric data stem from ref 9.

clusters, which consist of approximately six segments only. That interpretation of the gel transition is in accord with published ideas[5-7,21] concerning the "local melting" of intersegmental contacts.

In view of this model it is easily conceivable why the heat effects indicating gelation in DSC experiments fade out as the fraction of solvent approaches zero: The more concentrated the solution becomes, the higher the functionality of a cross-linking site will be, since it eventually contains only segments that all belong to different molecules. For that reason the number of cross-links per volume at the gel point will decrease and the effects become very small.

The picture of physical cross-links made up by the *n*-butyl side groups of the polymer is also compatible with the results of the DRS experiments. The reduced mobility of the dipoles that are situated within such a cluster of segments at $T < T_{gel}$ manifests itself in higher activation energies for the $\alpha\beta$-process. This observation is in agreement with dielectric studies[22] of isotactic poly(methyl methacrylate) dissolved in toluene. That system is similar to the one studied here in the sense that the physical cross-links do not consist of crystallites, as confirmed by X-ray measurements. For gels of other poly(*n*-alkyl methacrylates) with longer side chains, where gelation is assumed to be due to side-group crystallization, the gel/sol transition is indicated[23,24] by a sharp drop in $\epsilon'(T)$ at T_{gel}. The absence of such an effect with the system 2-POH/PBMA 520 agrees with the present picture of the cross-linking sites.

On the basis of the present experimental material, some speculations can be made concerning the question as to why the pure polymer does not gel, in contrast to the solutions, and how this phenomenon is made possible by the presence of solvent. The main clue stems for the observation that the gelation temperature extrapolated for the pure polymer by means of the best nonlinear fit from the data points in Figure 9 and the splitting of the $\alpha\beta$ process into two distinguishable processes shown in Figure 6 coincide within approximately ±2 °C. This can be taken as an indication that this partial freezing-in of motion, which remains inconsequential for the flow behavior of the pure polymer, is drastically amplified by the presence of the solvent. One reason for this effect could be that the system has now the opportunity to choose amongst the different types of contacts between the hydrophobic and hydrophilic groups of the polymer on one side and the solvent on the other. As a result of the optimization of the Gibbs energy, in which the free volume introduced by the solvent should play a decisive role, the energetically very favorable intersegmental clusters forming the cross-linking sites can be built up.

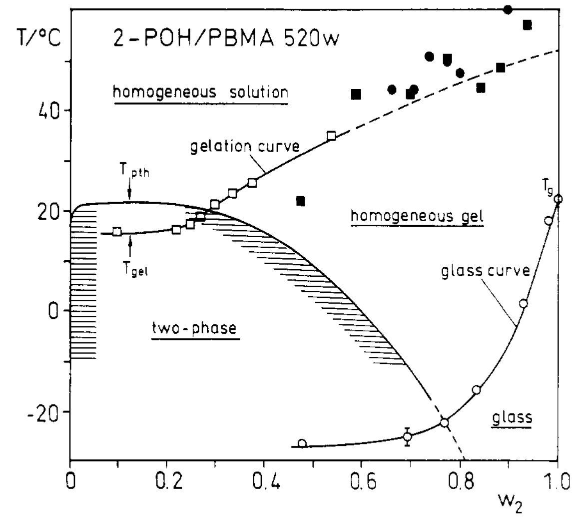

Figure 10. Phase diagram of the system 2-POH/PBMA 520. Glass transition temperatures T_g are measured by DSC (open spheres). Gelation temperatures T_{gel} stem from studies by viscometry[29] (open squares), DSC (full squares), and DRS (full circles). The hatched area indicates the visually determined miscibility gap; the measuring points, mostly taken from ref 29, are omitted for the sake of clarity; T_{pth} is the precipitation threshold.

Glass transition temperatures: The T_g values of pure polymers are reduced by the addition of low molecular weight components in the normal way. Qualitatively, 2-POH acts on PBMA just like any other plasticizer; the function $T_g(w_2)$, however, deviates considerably from additivity as formulated in eq 3, as shown in Figure 4.

The most probable explanation for this behavior is provided by the fact that polymer/polymer contacts are preferentially (i.e., in larger number than required by statistics) already formed at comparably high temperatures far from the demixing for thermodynamic reasons. This leads to a local increase in polymer concentration over the average value (for more details cf. ref 9) and to a behavior that would be predicted for truly homogeneous solutions only at higher w_2 values.

A theoretical description of $T_g(w_2)$ beyond that of eq 3 has to take account of the thermodynamic interactions between the components and of their differences in the fraction of the free volume. Numerous approaches have been published in the literature,[25] none of them can, however, be applied to the present system without several adjustable parameters. By means of the following empirical modification and extension of eq 3, the measured concentration dependence of T_g can be well reproduced

$$1/T_g = (\varphi_1/T_{g1} + \varphi_2/T_{g2})(1 - k\varphi_1\varphi_2) \qquad (5)$$

by setting the constant k equal to unity.

Phase diagram: The results of all measurements with the present system are collected in Figure 10. It demonstrates that the concentrated polymer solutions of particular interest solidify upon a reduction of temperature in two steps.

If the homogeneous still liquid solutions are cooled, the solvent quality is reduced to an extent that would already lead to phase separation at lower polymer concentrations.

Under these conditions the contacts between the polymer chain and the solvent molecules become energetically so unfavorable that the segments start to form clusters that become larger and more numerous as T is lowered, in spite of the entropical cost associated with that procedure. As soon as the gelation temperature is reached, a macroscopic and sufficiently long-lived network is formed; according to that said above, its existence is bound to the presence of solvent.

Below T_{gel} the just-described processes should go on: i.e., the number of cross-links and the number of segments they consist of are expected to increase. Although these changes will raise the stiffness of the gel, the mobility of the many segments separating the clusters is much higher than that in the glassy state as revealed by the DSC experiments. The solutions have to be cooled down well below the glass transition temperature of the pure polymer before this motion also freezes in and the glass curve is reached.

Although gelation and glass transition are different processes, as just outlined, they should not be independent of each other. The gelation of the present solutions appears only possible due to the fact that the thermodynamic mixing conditions, which favor the formation of cross-links, are realized in the proximity of the glassy solidification of the pure polymer. In this temperature regime, the mobility of the segments is already comparatively low for highly concentrated solutions and the enthalpic preference of intersegmental contacts suffices for a solidifcation of the system. On the other hand, the glass transition of the already gelled polymer solutions is shifted toward higher temperatures as compared with normal systems due to the reduction of chain mobility caused by the physical cross-links. This observation can also be interpreted as chain stiffening similar to the increase of T_g with increasing cross-linking density, as has been found for example for epoxy resins.[26,27]

Outlook

Although the above statements appear plausible, they do not yet explain why gelation is observed with the solutions of PBMA in 2-POH but, for instance, not with *n*-decane as the solvent, despite the fact that both systems demix upon cooling. In view of published thermodynamic studies on the co-occurrence of phase separation and thermoreversible gelation, it has to be expected that differences in the heat of mixing of the components are decisive. Only if this quantity is sufficiently large at a given temperature does it suffice to establish the long-lived intersegmental contacts that are required for gelation. This hypothesis is currently being tested.

Furthermore, NMR studies with the system 2-POH/PBMA are under way (Projekt D 9, SFB 262) in order to obtain information on the changes in the mobility of the side groups of the polymer associated with the formation of cross-links and with the glassy solidification.

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