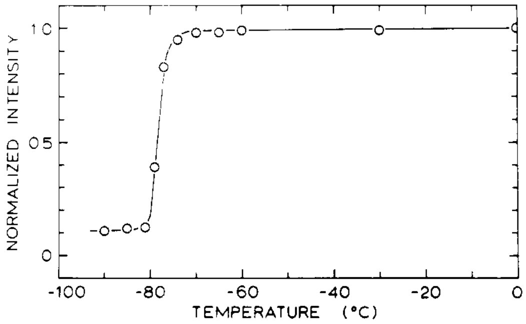

Figure 3. Normalized integrated peak intensity of PDMS, relative to the methyl group intensity of toluene, as a function of temperature.

rapidly below −70 °C, vanishing almost completely at −80 °C. The small peak which remains is due to low molecular weight species present in the sample and is indicated by the arrow in Figure 2. This behavior, which is reversible, is indicative of a disorder–order transition, i.e., crystallization of PDMS. The "crystallization temperature" is relatively sharp. However, the phenomenon is rate-dependent; i.e., it depends on the time allowed for equilibration at each temperature.[11]

Both NMR and X-ray measurements show that the crystallization of PDMS from solution in toluene occurs between −75 and −90 °C. It should be noted that this temperature is much lower than the temperature of −37 °C, corresponding to the UCST, predicted for the PDMS + toluene system by Kuwahara et al.[5] It is seen from Figure 3 that there is no indication of a phase separation in the region from −30 to −40 °C, nor was there any visual evidence of phase separation above −75 °C.

Conclusions

It has been shown that the crystallization of PDMS from solution occurs between −75 and −100 °C. The interplanar spacings for the solution-crystallized PDMS and the cross-linked silicone rubbers are identical. The lower the molecular weight, the greater is the degree of crystallization, as can be seen from the number of reflections recorded in Figure 1. The results indicate that crystallization of PDMS from solution is a bulk phenomenon and not surface-induced as was previously suggested.[6] It would also appear that the Θ temperature predicted in the literature for the PDMS + toluene system should be reevaluated.

Acknowledgment. We are indebted to Dr. M. L. Hair for interesting discussions and to L. C. Campbell for recording the low-temperature X-ray patterns.

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Thermally Stimulated Depolarization of Phase-Separated Polymer Systems

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ABSTRACT: The thermally stimulated depolarization method has been used to study the relaxation behavior of the two block copolymers poly(styrene-*b*-butadiene) and poly(ϵ-caprolactone-*b*-styrene) and the polyblend poly(methyl methacrylate)–poly(*tert*-butyl acrylate). The relaxation peaks resulting from molecular local motions or glass transition are similar to those observed in pure homopolymers, showing that a well-defined phase separation occurs in these systems. In addition, peaks due to interfacial polarization are obtained where the constituent phases possess markedly different electrical conductivities while no evidence is found for a relaxation effect requiring the existence of a diffuse interface between the microdomains.

It is known that the relaxational behavior of block copolymers and polyblends in the solid state is largely determined by their microdomain morphology: if the boundary between phases is sharp, the molecular relaxation spectrum can be, in principle, strictly described by a superposition of the spectra of the two pure homopolymers; if a more or less important amount of molecular mixing is taking place, the transitions are generally broadened, their maximum temperatures are closer together, and new relaxation peaks may appear. In these conditions, a current and essential problem encountered in the study of the multiphase systems is to determine the cause and nature of the influence of one particular material on the other's relaxation. With this in view, dynamic mechanical characteristics, mostly in the form of the temperature response of shear or Young's modulus and mechanical loss, have been used with considerable success.[1-3] The dielectric measurements, in particular the temperature dependence of dielectric constant and losses, were also shown to be a useful means for characterizing the nature of phase separation because they allow not only the fol-

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Table I
Characteristics of Poly(ϵ-caprolactone-*b*-styrene) Copolymers

code	compn[a]	$10^{-3}\bar{M}_n$[b]	% crystal-linity[c]	melting temp, °C
SC1	30	140	40	60
SC2	47	87	36	59
SC3	51	78	32	58
SC4	74	54	0	55

[a] Wt % of styrene. [b] Determined by osmotic pressure. [c] Degree of crystallinity determined by differential scanning calorimetry.

lowing of any deformation or shifting of the relaxation peaks as in the mechanical case but also the possibility of observing a Maxwell–Wagner–Sillars effect (MWS) due to trapping of charge carriers at phase boundaries.[4] However, the MWS losses are only apparent for low measuring frequencies, usually below 1 Hz, i.e., frequencies which are still difficult to obtain experimentally by conventional bridge methods. It seems, therefore, that the thermally stimulated depolarization technique (TSD), which commonly works in ranges of equivalent frequencies of 10^{-2}–10^{-4} Hz,[5,6] could be revealed as a useful complementary tool for the dielectric study of such materials.

In the framework of a general investigation aimed at testing the ability of the TSD method for studying the relaxational properties of heterogeneous systems, we report in this paper the results obtained in styrene–butadiene block and random copolymers, styrene–ϵ-caprolactone block copolymers, and a methyl methacrylate–*tert*-butyl acrylate polyblend.

Experimental Section

Materials. Styrene–butadiene teleblock copolymers (SB), Solprene 406, 411, and 415, were supplied by Phillips Petroleum. Their total styrene contents, determined by the method of Kolthoff et al.,[7] were 38, 31, and 41 wt %, respectively, and molecular weights $\bar{M}_n$, obtained by gel permeation chromatography, were 162.000, 195.000, and 123.000, respectively.[8] These copolymers contain trans, cis, and vinylbutadiene units (approximately 50, 40, and 10 wt %, respectively, of the total butadiene content, as determined by IR spectrometry).[8]

Styrene–butadiene random copolymers (SBR), Synpol 8107, 1061, and 8000, with total styrene contents of 6, 24, and 43 wt % and $\bar{M}_n$'s of 90.000, 140.000, and 100.000, respectively, were supplied by Texas-U.S. The proportions of trans, cis, and vinylbutadiene units were 68, 15, and 17 wt %, respectively, of the total butadiene content. These copolymers, which originally contain small amounts of stabilizer, emulsifier, and coagulant, were purified before use by reprecipitating with methanol from benzene.

The poly(ϵ-caprolactone-*b*-styrene) copolymers (CS) were prepared in the laboratory from modified μ-oxo-aluminumzinc alkoxide catalysts as described elsewhere.[9] They are free of homopolymers and their total styrene contents, determined by NMR, varied from 30 to 74 wt %. Their characteristics are listed in Table I.

Poly(methyl methacrylate) (PMMA) and poly(*tert*-butyl acrylate) (P-*t*-BA) were prepared by radical polymerization in benzene with benzoyl peroxide and α,α'-azobis(butyronitrile), respectively, as a catalyst. After purification, they were simultaneously dissolved in toluene and reprecipitated with methanol.

Sample Preparation. Samples for TSD measurements were obtained in the form of flat uniform disks, 70 mm in diameter and 1 mm thick, by compression molding at 60 (SBR), 100 (CS), or 150 °C (SB and PMMA-P-*t*-BA). They were provided with two measuring electrodes and a guard ring either by evaporating aluminum under vacuum or by painting with colloidal silver and then were vacuum-oven dried over phosphorus pentoxide at temperatures higher than the glass transition temperature for at least 1 week. It was thought that this treatment not only would remove residual moisture and solvents but would ensure that the polymers were free of residual stress which is known to sometimes affect the TSD results.

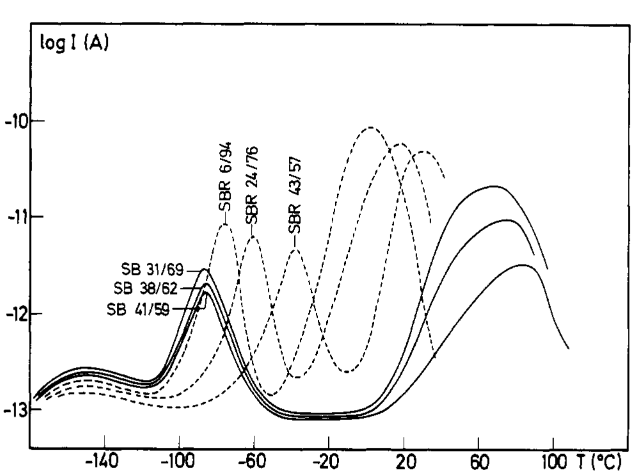

Figure 1. TSD spectra of styrene–butadiene block and random copolymers.

TSD Measurements. The experimental device used for recording the thermally stimulated depolarization currents is a classical one and has been described in a previous paper.[10] The thermal cycles of polarization and depolarization consist essentially of the following steps: (1) heating to a temperature T_p higher than the upper glass transition temperature T_g of the polymer investigated; (2) application of a dc electric field E_p (=10–30 kV/cm) for a time t_p (=10–60 min); (3) rapid cooling in the field to a temperature $T_0 \ll T_p$; (4) cutting off the external field and linear heating of the short-circuited samples at a rate b (=5 °C/min).

Results and Discussion

1. Styrene–Butadiene Copolymers. Figure 1 shows the TSD spectra of styrene–butadiene block (solid lines) and random (dashed lines) copolymers polarized at 110 (SB) or 60 °C (SBR) in a dc field of strength E_p = 12 kV/cm during a time t_p = 30 min. All have the same general shape and are characterized by three distinct current peaks which are conventionally labeled β, α, and ρ in order of increasing temperatures.

β Peaks. These peaks, usually asymmetrical and widely spread between −180 and −100 °C, are probably composed of two or more overlapping, poorly resolved peaks. Since their positions seem to be little affected by the copolymer structure while their amplitudes are decreasing functions of the styrene content, they can be related to local motions of butadiene units. Similar low-temperature complex transitions have been observed in pure polybutadiene by dynamic mechanical measurements[11] and are ascribed to relaxations involving only the trans units of the polymers. This explanation, however, cannot hold for the TSD peaks since the trans isomer is dielectrically inactive[12,13] and the maximum intensities are higher in SBR samples (68% trans units) than in SB samples (50% trans units).

α Peaks. The α peaks of the random copolymers always appear close to the glass transition temperature as determined by differential scanning calorimetry (DSC) and shift similarly as a function of the styrene content (Figure 2). Such behavior can be well represented by the Gordon–Taylor copolymer equation,[14] which is in agreement with literature data.[15] The existence of a strict proportionality between the maximum intensity of the peaks I_{M_α} and field strength (Figure 3) shows that a uniform volume dipolar polarization is taking place; this is confirmed by the fact that I_{M_α} is also a linearly increasing function of the butadiene content (Figure 4). It thus seems that these peaks can be ascribed to micro-Brownian motions of chain

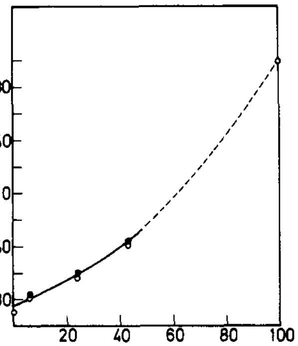

Figure 2. Variation of T_g (○) and T_{M_α} (●) with composition for the styrene–butadiene random copolymers.

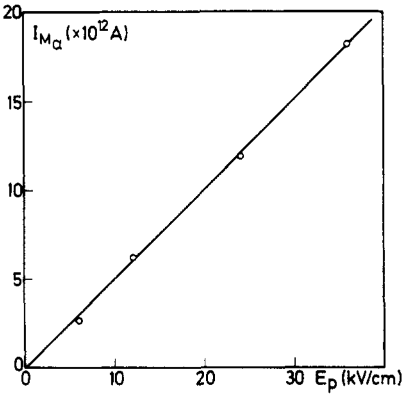

Figure 3. Variation of I_{M_α} with electric field strength for a styrene–butadiene random copolymer with a styrene content of 24 wt %.

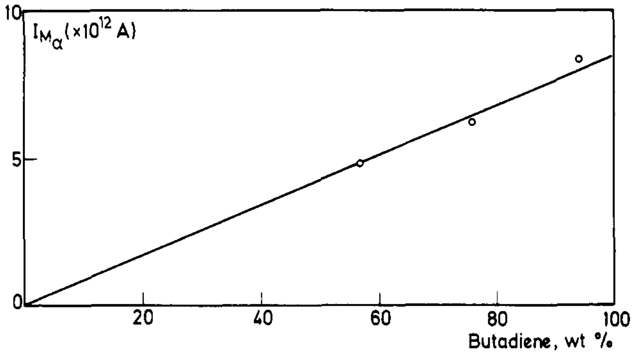

Figure 4. Variation of I_{M_α} with composition for the styrene–butadiene random copolymers.

segments involving rotation of cis and vinylbutadiene isomers (effective dipole moment = 8.2×10^{-31} Cm).[4]

In the block samples, the α peaks have maximum temperatures close to the glass transition temperature of pure polybutadiene ($T_g \simeq -90$ °C for 15% vinyl) and can thus be attributed to micro-Brownian motions occurring only in the elastomeric phase. They do not significantly shift when the copolymer composition varies, which is obviously a good indication of the existence of a well-defined two-phase structure. Moreover, the lack of any relaxation in the temperature range corresponding to the α relaxation of the random copolymers ($-60 \rightarrow +20$ °C) shows that any mixing of styrene and butadiene segments at the phase boundaries is not detectable as a distinct dispersion region, which is in agreement with recent dielectric studies of North et al. in styrene–butadiene–styrene triblock copolymers.[4] Obviously, this does not necessarily mean that a diffuse interface is not present but only that no argument for its existence can be found from such TSD data.

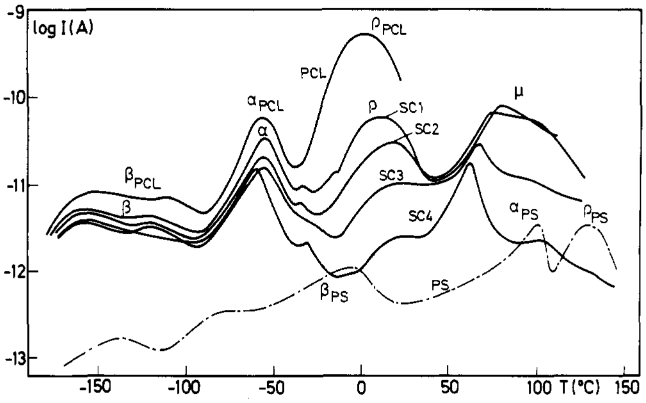

Figure 5. TSD spectra of poly(ϵ-caprolactone), polystyrene, and poly(ϵ-caprolactone-*b*-styrene) copolymers.

ρ Peaks. The high-temperature peaks of the random copolymers do not seem related to any known intrinsic relaxation. On account of their high intensity and area, on one hand, and the marked influence exercised by doping, water sorption, and thermal history,[16] on the other, they probably result from a polarization process involving charge-carrier migration over macroscopic distances (space charge polarization). As with the α peaks, these ρ peaks shift toward higher temperatures with increased styrene content; this is a logical feature since the ionic mobility may be expected to be high only at temperatures higher than the glass transition temperature.

The ρ peaks of the block specimens do not correspond to any intrinsic transition of polybutadiene or polystyrene entities and show also properties typical of ionic processes. However, due to the heterogeneous character of the copolymer structure and the marked differences between the electrical conductivities of the constituent phases ($\sigma \simeq 10^{-17}$ and 10^{-21} Ω^{-1} m^{-1} for pure polybutadiene and polystyrene, respectively), the TSD peaks must be correlated with an interfacial polarization of the MWS type rather than a space charge polarization. This is confirmed by the good agreement observed between the peak positions and the temperatures where the mobility of the polystyrene regions increases substantially as proved, for example, by abrupt decreases in tensile strength[17] or in the stress-optical coefficient of similar copolymers.[18]

In principle, an additional peak of the α type should appear in block copolymers near the glass transition temperature of the polystyrene phase ($T_g \simeq 100$ °C). The fact that it is not detectable in the TSD spectra is likely to result from the masking effect exercised by the high-amplitude ionic process.

2. Poly(ϵ-caprolactone-*b*-styrene) Copolymers. The TSD spectra of these copolymers are represented in Figure 5, together with the spectra of the two pure homopolymers. They are composed of four distinct regions, which are labeled β, α, ρ, and μ in order of increasing temperatures. It seems obvious from the large dipole moment of the carbonyl bond ($\simeq$2.5 D) that most of the currents observed in the copolymers can be attributed to processes occurring either in the PCL phase or at the phase boundaries. This is confirmed by the fact that the depolarization currents of the two pure homopolymers differ by more than 2 orders of magnitude (Figure 5).

β Peaks. In spite of its clearly structured nature, the low-temperature region has been designated with the single conventional sign β, for it corresponds well to the β unresolved loss peak observed in pure PCL from mechanical experiments.[19,20] Moreover, detailed TSD studies on several PCL samples varying in crystallinity have shown that the two components (β_1 and β_2) probably result from the

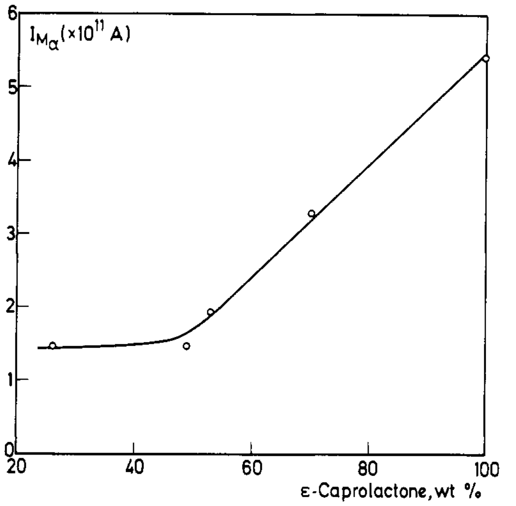

Figure 6. Variation of I_{M_α} with composition for the poly(ε-caprolactone-*b*-styrene) copolymers.

same crankshaft-type motion taking place in the amorphous and crystalline phases, respectively.[21] The disappearance of β_2 in the fully amorphous SC 4 copolymer (Table I) is further confirmation of this assumption.

α Peaks. The maximum temperature of the TSD α peak corresponds well to the glass transition temperature of poly(ε-caprolactone) determined from stiffness–temperature curves or by means of mechanical measurements on a series of compatible polymer mixtures[19] (−60 °C) and remains remarkably constant for caprolactone contents higher than 50 wt %, unambiguously proving that these copolymers are two-phase systems. A significant shifting of the α peak is apparent only in the amorphous sample with a styrene content of 74 wt %, since, as lower temperatures are approached, such a shifting cannot result from an increase in molecular mixing of the two phases but must rather result from the drastic decrease in crystallinity of the poly(ε-caprolactone) phase (Table I).

The maximum amplitude I_{M_α} is strictly proportional to the field strength but is not a monotonously increasing function of the sample composition (Figure 6), owing to the simultaneous variations in the degree of crystallinity. The TSD α peak can thus be ascribed to a dipolar polarization associated with micro-Brownian motions in the amorphous poly(ε-caprolactone) phase.

The weak shoulders appearing in the decreasing part of the α peaks (Figure 5) are hardly reproducible and their characteristics are greatly influenced by external factors such as water sorption. These peaks are thus to be ascribed to some easily ionizable impurity rather than to a new dispersion resulting from molecular mixing.

ρ Peaks. These peaks do not correspond to any intrinsic transition of the constituent homopolymers and are markedly affected by doping or water sorption,[16] providing evidence for an ionic process of the MWS type. Since yet present in the fully amorphous copolymer SC4, this process probably results from charge carriers piled up at the polymer–polymer interfaces rather than at the boundaries between crystallites and amorphous regions of the poly(ε-caprolactone) phase. The systematic variation in position and amplitude of the ρ peaks as a function of the styrene content may then be related to a decrease in ionic mobility following the progressive change of a continuous PCL phase ($\sigma \simeq 10^{-15}\ \Omega^{-1}\ \mathrm{m}^{-1}$) into a continuous PS phase ($\sigma \simeq 10^{-21}\ \Omega^{-1}\ \mathrm{m}^{-1}$).

μ Peaks. The complex μ peaks appear between 50 and 100 °C, i.e., in the melting range of the poly(caprolactone) phase and thus, probably result from large-scale motions

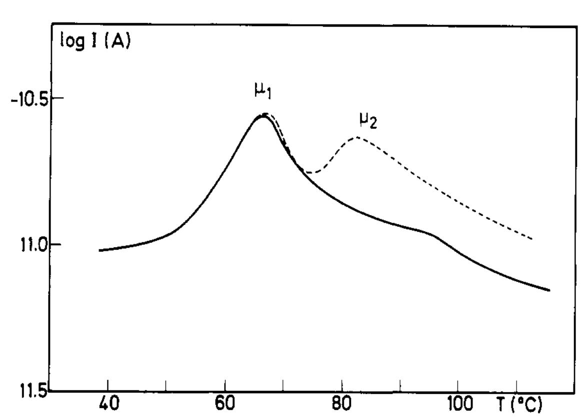

Figure 7. Influence of a variation in polarization conditions on the melting TSD region of a poly(ε-caprolactone-*b*-styrene) copolymer with a caprolactone content of 49 wt % (see text).

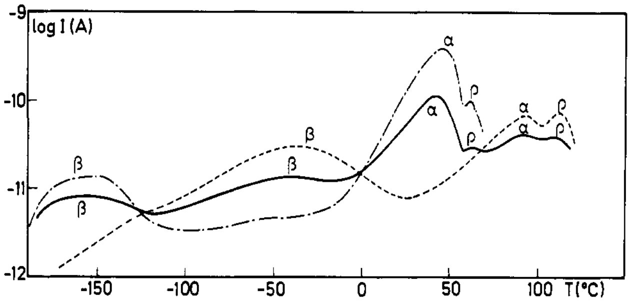

Figure 8. TSD spectra of PMMA (- - -), P-*t*-BA (-·-), and a 40/60 PMMA–P-*t*-BA polyblend (—).

of molecular dipoles as well as from recombinations of ions previously trapped into the crystallites during the cooling process. These two phenomena were distinguished by studying the influence of a variation in polarization conditions on the copolymer containing 49 wt % poly(caprolactone) (Figure 7). In a first step, the sample was polarized under usual conditions (rapid cooling from +120 to −196 °C) (solid line) while in a second step, polarization was obtained by slow cooling from 120 to 100 °C, followed by a rapid cooling up to −196 °C (dashed curve). This last procedure does not affect the mode of crystallization and thus the dipolar mobility into or around the crystallites but changes markedly the ionic polarization by allowing a more effective charge separation. It follows that the first, unaffected peak (μ_1) can be ascribed to the dipolar relaxation mechanism and the second, enhanced peak (μ_2) to an ionic process.

In most of these copolymers, the expected TSD peak corresponding to the glass transition of the weakly polar polystyrene phase is obviously masked by the μ peaks. Only in the copolymer with high styrene content (SC 4) could the shoulder appearing near 100 °C be related to an α process; its final attribution will require still more experimental evidence.

3. Methyl Methacrylate–*tert*-Butyl Acrylate Polyblend.

The TSD spectra of acrylic polymers such as PMMA and P-*t*-BA are now well-known, having been reported and analyzed by many authors.[5,22-24] They are generally composed, between −150 and +150 °C, of three overlapping peaks which are conventionally labeled β, α, and ρ in order of increasing temperatures and may be respectively ascribed to local motions of ester side groups (β relaxation), micro-Brownian motions of main-chain segments (glass transition or α relaxation), and space charge polarization (ρ).

As seen in Figure 8, the TSD spectrum of an optically transparent polyblend composed of 40 wt % PMMA and

60 wt % P-*t*-BA is clearly a superposition of the spectra of the two pure homopolymers, thus revealing a high degree of incompatibility at the microscopic level. On the other hand, no additional MWS peak is detectable, probably because the constituent phases possess similar electrical conductivities.

Conclusions

The shape and position of the molecular relaxation peaks appearing in block copolymers and polyblends studied in this paper are generally similar to those observed in the pure constituent homopolymers while no relaxation effect ascribable to a possible diffuse interface has been detected. These results, although not disproving the existence of such a diffuse boundary, show that the amount of molecular mixing, if any, is weak and that the relaxations involving ionic charge carriers are to be attributed to interfacial polarization resulting from the existence of well-separated phases rather than to space charge polarization. The present experimental evidence thus suggests that the thermally stimulated depolarization technique is well suited to the study of the relaxational behavior of heterogeneous materials. Obviously, several problems remain to be solved for a quantitative analysis of the spectra in terms of phase volumes and microdomain morphology. This will be the subject of a further paper.

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Aging and Thermodynamics of Polyacrylamide Gels

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ABSTRACT: Arguments that the large changes observed in the swelling of polyacrylamide gels "cured" for different lengths of time are due to the formation of a heterogeneous structure rather than an increase in cross-link density as was recently suggested are presented. Torsion pendulum measurements indicate that the effective cross-link density remains practically constant over a period of 40 days. To interpret the swelling data we use a simple two-phase model which despite its simplicity reproduces reasonably well the experimental data and indicates that the aging phenomenon may be the result of the development of such a heterogeneous structure.

The thermodynamics of gels describe the swelling or collapse phenomena that are observed when a gel network is brought into contact with a solvent. The underlying idea, due to Flory,[1] is the interpretation of the swelling equilibrium as an osmotic pressure equilibrium of the solvent outside and inside the gel network. Flory's equation predicting swelling of *dry* gels in good solvents has been tested with good agreement on various systems, including natural rubber,[2] butyl rubber,[3] and polystyrene gel.[4] For gel networks which are formed in the presence of a solvent, Hermans'[5] or Dušek's[6] modifications of Flory's equation are commonly used. Recently, Tanaka[7] proposed an equation for the osmotic pressure of a gel–solvent system which was thought to have the unique feature of a sharp collapse (transition) as a function of polymer–solvent interaction (or temperature) when the gel possesses a cross-link density above a certain critical value. Such a sharp transition from swelling to collapse over a very narrow range of polymer–solvent interaction (or temperature) was observed by Tanaka for *aged* polyacrylamide gels in water–acetone mixtures as a function of acetone concentration, and more extensive results are presented below. The sharp transition exhibited by Tanaka's equation is not unique to that equation, and Hermans' (or Dušek's) equation exhibits a similar behavior,[8] although at higher values of the interaction parameter, χ, where χ is taken to be equal to $\Theta/2T$, with Θ being the Flory temperature of the polymer–solvent system. There are, how-

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