Enthalpy Relaxations in Blends of Polystyrene and Poly(2-vinylpyridine)

Rony Grooten and Gerrit ten Brinke*

Department of Polymer Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands. *Received July 15, 1988; Revised Manuscript Received September 27, 1988*

ABSTRACT: The enthalpy relaxation method proposed by Ellis and ten Brinke[1] for investigating miscibility in blends of polymers with a similar glass transition temperature (T_g) is applied to mixtures of polystyrene (PS) and poly(2-vinylpyridine) (P2VP). Both polymers are known to be immiscible, but despite the fact that the respective T_gs are 6 °C apart, only a single specific heat jump is visible in a conventional differentional scanning calorimetry (DSC) experiment. Physical aging at suitable temperature gives rise to two clearly separated enthalpy recovery peaks in the first DSC scan, thereby demonstrating the two-phase morphology. These experiments together with theoretical considerations based on Moynihan's approach will be used to formulate conditions for a successful application of the enthalpy relaxation method.

Introduction

In recent years considerable progress has been made concerning our understanding of the basic principles underlying miscibility in polymer blends. The role of specific interactions, once thought to be indispensable, has in many cases been taken over by the intramolecular repulsion effect.[2-4] Even when specific interactions are known to be present, the situation is often dominated by this repulsion effect.[5,6] Most of our improved insight results from a systematic study of phase behavior in polymer mixtures involving large classes of closely related polymers. Miscibility is often most conveniently determined by calorimetric measurements using the well-known single composition dependent glass transition temperature (T_g) criterion. The onset of phase separation in blends of polymers which are miscible at a particular temperature is located by annealing at various temperatures above T_g, followed by a rapid quench to ambient temperature and subsequent thermal analysis at 10 or 20 °C/min. This measurement when performed by DSC then reveals either one or two discontinuities in the heat capacity, according to whether or not phase separation has taken place. A prequisite for this procedure to work is that the T_gs of both components are sufficiently far apart. If this is not the case different methods have to be used. A number of alternatives are available and described in some detail in the literature.[7] However, very recently we have demonstrated that calorimetric methods remain a valid experimental technique even when the T_gs of the polymers are very close to each other.[1] The procedure relies on the phenomenon of enthalphy recovery in physically aged glassy blends.

Before we go into details of the method, a short introduction of the Hodge and Berens[8] extension of Moynihan and co-workers'[9,10] original approach of the phenomenology of the glass forming kinetics will be given. Other approaches available are the KAHR model,[11] the coupling model of Ngai,[12] and the Robertson-Simha-Curro theory.[13] Many details of these models can be found in the excellent collection of papers published as *Relaxations in Complex Systems*, edited by Ngai and Wright,[14] and in a forthcoming review article by McKenna.[15] We are mainly interested in the enthalpy relaxation which occurs during physical aging and the subsequent enthalpy recovery which occurs during reheating. Since Hodge and Berens have applied their approach extensively to these types of experiments, using differential scanning calorimetry (DSC), we will focus on it, although there are indications that the coupling model is in some respects more accurate.[16]

The enthalpy relaxation which occurs during annealing at temperatures T_a below the glass transition temperature T_g is nonexponential and nonlinear. The modeling of these properties is based on earlier work by Tool[17] and Narayanaswamy and Gardon.[18,19] The relaxation toward equilibrium of the enthalpy H is described by a relaxation function $\phi(t)$:

$$\frac{H(T_a,t) - H(T_a,\infty)}{H(T_a,0) - H(T_a,\infty)} = \phi(t) \qquad (1)$$

where $H(T_a,t)$ is the value of the enthalpy after annealing during a time t at temperature T_a.

Within Moynihan's approach $\phi(t)$ is given by the William-Watts form

$$\phi(t) = \exp(-(t/\tau)^\beta) \qquad (2)$$

where $0 < \beta \leq 1$ is a measure of the width of the relaxation spectrum, as follows from the first moment $\langle t \rangle$ of this function which is given by[20]

$$\langle t \rangle = \frac{\tau}{\beta}\Gamma(1/\beta) \qquad (3)$$

where Γ is the gamma function. Besides the nonexponentiality expressed by eq 2 for $\beta < 1$, the enthalpy relaxation is also nonlinear in the sense that the average relaxation time is structure dependent. It is introduced by making the relaxation time τ an explicit function of the fictive temperature T_f introduced by Tool[17]

$$\tau = A \exp\left[\frac{x\Delta h^*}{RT_a} + \frac{(1-x)\Delta h^*}{RT_f}\right] \qquad (4)$$

T_f is defined as the temperature at which the observed property would be the equilibrium value (Figure 1), x is the nonlinearity parameter, Δh^* an activation enthalpy, A a preexponential factor, and R the ideal gas constant.

As stated before, the conventional single compositional dependent T_g criterion for miscibility in polymer blends is useless if both components have a similar T_g. Recent examples can be found in ref 21 and 22. In our latest publication[1] we proposed a related procedure based on enthalpy recovery of physically aged samples. First the system is brought to equilibrium in the melt at the temperature of interest. Next the system is quenched and annealed at a suitable temperature T_a below the glass transition temperature for a certain amount of time. The enthalpy relaxation that occurs at this stage is recovered during reheating and is visible as an endothermic peak in

0024-9297/89/2222-1761$01.50/0

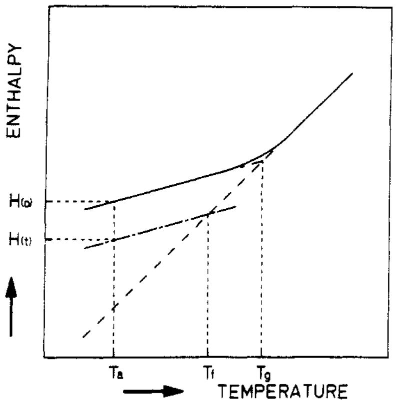

Figure 1. Illustration of the aging time, t_a, dependence of the fictive temperature T_f. $H(t)$ and $H(0)$ are the values of the enthalpy after annealing during a time t and without annealing at temperature T_a, respectively.

a DSC scan. The position of this peak depends on the thermal treatment given and on the structure of the material itself. Each polymer has its own individual aging behavior reflected in the position and magnitude of the recovery peak on heating through T_g. In ref 1 the method was demonstrated by investigating two different blends: an immiscible blend of poly(vinyl chloride) (PVC) and poly(isopropyl methacrylate) (PiPMA) and a miscible blend of PVC and poly(methyl methacrylate) (PMMA). Apart from having similar T_gs, PVC and PiPMA were chosen as a model system because literature data suggested a considerably different aging behavior of these components. In particular, PVC was known to show enthalpy recovery peaks well below the glass transition temperature.[23-25] Sub-T_g peaks are a consequence of the memory effect, which in turn implies that the value of β in the relaxation function given by eq 2 has to be smaller than 1.[20] The memory effect describes the observation that the relaxation in a particular state depends not only on this state but also on how it was reached. A classic example is the volume maximum observed as a function of time after two temperature steps of opposite sign in the glassy regime.[26]

In ref 1 we demonstrated that the thermograms of aged blends of PVC and PiPMA showed two very distinct endothermic peaks associated with two phases. By comparing these peaks with those of the pure components we concluded that phase separation had taken place and that the composition of the two phases in equilibrium with each other was nearly pure PVC and PiPMA. Because the aging behavior of PVC and PiPMA was expected to be and turned out to be quite different, it remained to be seen whether the procedure would also work for polymers for which a more comparable aging behavior could be expected. To this end we decided to investigate mixtures of polystyrene (PS) and poly(2-vinylpyridine) (P2VP). Both polymers have similar glass transition temperatures and were predicted to be immiscible by Shaw,[27] based upon ternary (two polymers, one solvent) phase behavior using methylene chloride as the solvent. The enthalpy relaxation behavior of polystyrene has been investigated before[28,29] but not in relation to poly(2-vinylpyridine) for which no data are available yet.

Experimental Section

Polystyrene was a commercially available product obtained from Dow (Styron 666). Poly(2-vinylpyridine) was synthesized in our laboratory by J. Smid. Both polymers were purified by precipitation from dilute chloroform solutions (5 wt %) into a 30 times excess of n-hexane. Next the samples were dried under vacuum at 50 °C for at least 1 week. The molecular weights were determined by GPC (Waters ALC/GPC 150 c) using tetrahydrofuran (THF) as an eluent. Values of M_w and M_n were calculated relative to polystyrene standards. Thermal analysis was performed with a Perkin-Elmer differential scanning calorimeter (DSC-7) at a heating rate of 20 °C/min. The onset glass transition temperatures were measured as the point of intersection of the extrapolated baseline with a line drawn through the point of inflection of the incremental change in heat capacity. Onset T_gs and molecular weights are shown in Table I. Blends of P2VP and PS were obtained by coprecipitation from a 5 wt % chloroform solution into a 30 times excess of n-hexane. The composition of each blend was 50/50 wt %.

Table I
Molecular Weights and Glass Transition Temperatures

material	M_w	M_n	T_g, °C
PS	236 000	90 000	106
P2VP	93 000	41 000	100

Samples for aging were prepared by pressing the dry powder of the polymers into tablets. They were then sealed in small DSC pans under argon atmosphere. The sample weight varied between 8 and 21 mg. Most samples were kept at 140 °C for 5 min. Then the samples were cooled by quenching in liquid nitrogen, followed by aging for different amounts of time t_a at aging temperatures $T_a < T_g$. In most cases T_a was either 80 or 91 °C; t_a varied between 1 and 1027 h. Subsequently, a DSC scan was taken from −5 to 140 °C. Finally, after annealing at 140 °C for 5 min, the samples were quickly cooled to −5 °C (200 °C/min) and a second scan was taken.

Results and Discussion

The pure polymers PVC and PiPMA, investigated before,[1] had glass transition temperatures which were only two degrees apart. When aged at 60 °C, i.e., $\approx T_g - 20$ °C, both revealed the characteristic endothermic enthalpy recovery peaks on reheating. The difference between the respective maxima of the endotherms, T_{max}, turned out to be somewhere between 8 and 10 °C. As a consequence, the thermograms of the aged phase-separated blends showed two very distinct endothermic peaks. There is no reason to believe a priori that this enhanced difference will be found in other systems as well. The large difference between PVC and PiPMA might be related to small amounts of crystallinity in PVC, which obviously will influence the relaxation behavior.

The polymer pair PS and P2VP offers prospects for a more serious test of the enthalpy recovery method. The glass transition temperatures of approximately 100 and 106 °C (Table I) are 6 deg apart, which is still not large enough to observe two separate heat jumps in a conventional DSC scan of a phase-separated blend. To examine the enthalpy relaxation behavior samples of PS, P2VP, and mixtures of 50/50 wt % of PS and P2VP were prepared. They were uniformly exposed to a temperature of 140 °C for 5 min. For the first set of experiments the samples were subsequently aged at 80 °C for various amounts of time. Figures 2 and 3 show the thermograms for P2VP and PS, respectively. The aging times are indicated. In Figure 4 the positions of the respective maxima are given as a function of log (aging time). The linear relationship between T_{max} and log t_a observed is a well-known phenomenon when the aged glass is not too close to equilibrium.[20,30] In the same figure the onsets T_{ons}, of the enthalpy recovery peaks of P2VP and PS are also presented. As argued in ref 1, the position of the onset as a function of log t_a can give important additional information concerning the morphology of a two-component system. Usually the onset is also a linear function of log t_a.[1,32] In the case of P2VP, however, we observe a leveling off. This is, as will become clear, an indication that at aging times $t_a > 100$ h, P2VP is already close to equilibrium. For PS the linear relationship is

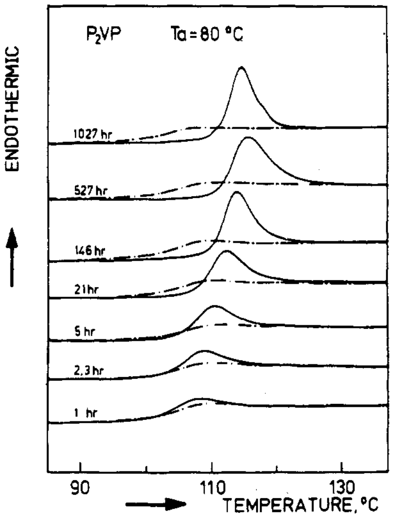

Figure 2. Thermograms of P2VP, quenched from 140 °C and aged at 80 °C for the times indicated: first scan (—); second scan (- - -).

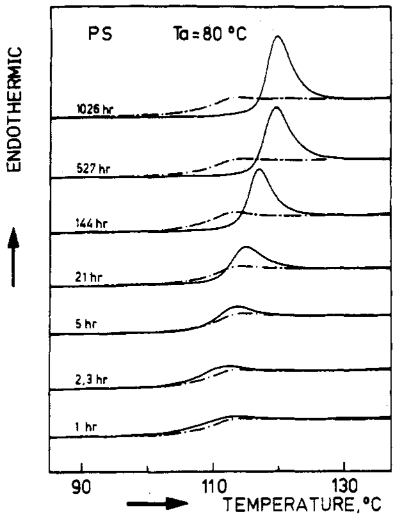

Figure 3. Thermograms of PS, quenched from 140 °C and aged at 80 °C for the times indicated: first scan (—); second scan (- - -).

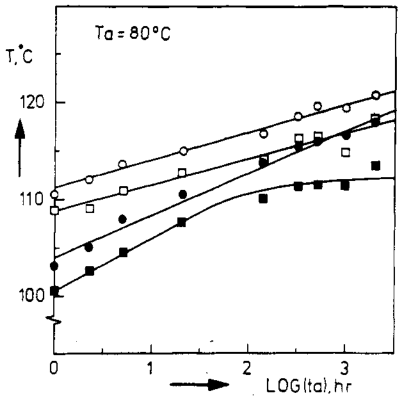

Figure 4. T_{max}, T_{ons} versus log t_a for P2VP and PS: (○, □) T_{max} of PS and P2VP, respectively; (●, ■) T_{ons} of PS and P2VP, respectively.

satisfied over the entire aging time regime investigated. At a given aging time the difference between the T_{max}s of the pure components is only 2–3 deg, i.e., clearly less than the difference between the T_gs.

Figure 5 shows the thermograms for the blends of P2VP and PS aged at 80 °C for the amounts of time indicated. Only one peak is observed. However, at relatively large aging times (t_a > 100 h) the shape of the endotherm is such that it seems to consist of two nearby peaks superimposed onto each other. This is confirmed by comparing the true maximum of the peak with the maximum of the peak of pure PS and the onset of the peak with the onset of the peak of pure P2VP. As demonstrated in Figure 6, the difference between these data is small, as expected for a phase-separated system. In particular, the leveling off at larger aging times of the T_{ons} of P2VP is also observed for the blend. That T_{ons} of the blend is slightly larger than T_{ons} of pure P2VP could be due to the P2VP-rich phase containing a small amount of PS. These results quite clearly demonstrate the importance of monitoring the position of the onset of the enthalpy recovery peak in addition to the position of the peak maximum. On the basis of these data alone, the conclusion concerning the presence of a two-phase morphology seems fully justified. The broken lines in Figure 5 correspond to the repeat scan taken immediately after cooling. These thermograms show a single continuous heat capacity change at T_g from which it is impossible to make a judgement with regard to the phase behavior of the blend. Although, as will become clear later, aging at 80 °C is far from the optimum condition, these experiments already demonstrate that as far as phase behavior is concerned, the enthalpy recovery method is more sensitive than the conventional single T_g criterion.

It is a well-established experimental fact reproduced by the Moynihan approach[8] that T_{max} increases linearly with

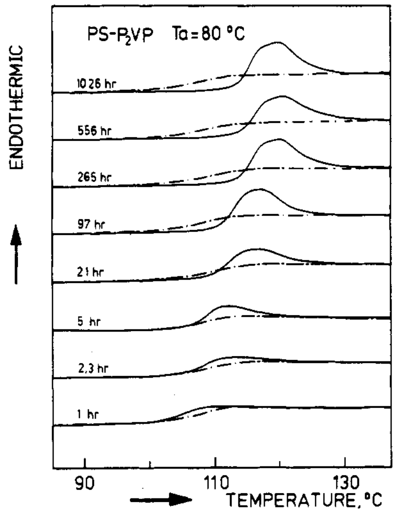

Figure 5. Thermograms of P2VP/PS, quenched from 140 °C and aged at 80 °C for the times indicated: first scan (—); second scan (- - -).

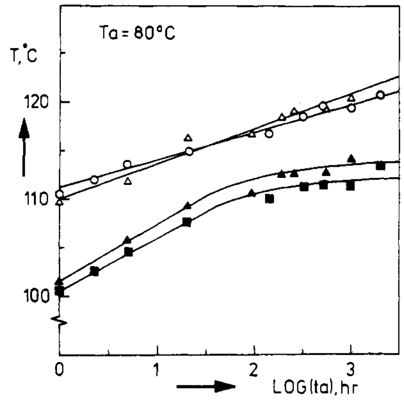

Figure 6. T_{max}, T_{ons} versus log t_a for P2VP, PS, and P2VP/PS: (○, △) T_{max} of PS and P2VP/PS, respectively; (■, ▲) T_{ons} of P2VP and P2VP/PS, respectively.

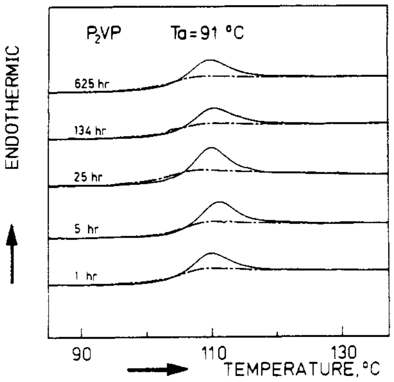

Figure 7. Thermograms of P2VP, quenched from 140 °C and aged at 91 °C for the times indicated: first scan (—); second scan (- - -).

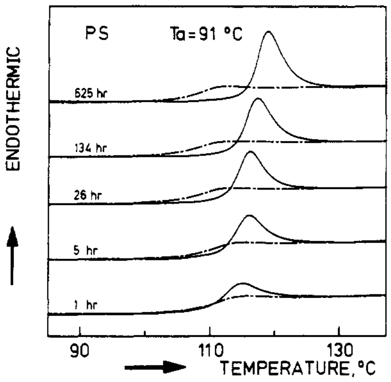

Figure 8. Thermograms of PS, quenched from 140 °C and aged at 91 °C for the times indicated: first scan (—); second scan (- - -).

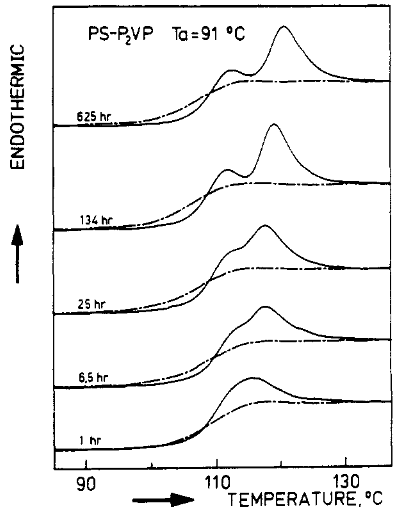

Figure 9. Thermograms of P2VP/PS, quenched from 140 °C and aged at 91 °C for the times indicated: first scan (—); second scan (- - -).

log t_a and with the aging temperature T_a as long as the aged glass is sufficiently far from equilibrium. The approach to equilibrium at a given aging temperature is determined not so much by the aging time as by the effective aging time[20]

$$t_{\mathrm{eff}} = t_a/\tau \tag{5}$$

where τ is given by eq 4. The preexponential factor A of the defining equation of τ is related to the relaxation time τ_0 at T_g by

$$\ln A = \ln \tau_0 - \Delta h^*/RT_g \tag{6}$$

For small values of t_a, the fictive temperature T_f coincides approximately with T_g, irrespective of the aging temperature T_a (cf. Figure 1). Therefore, the relaxation time τ at T_a is for small values of t_a given by[20]

$$\tau \simeq \tau_0 \exp \frac{x\Delta h^*}{RT_aT_g}[T_g - T_a] \tag{7}$$

From eq 5 and 7 we conclude that for polymers of similar relaxation behavior, i.e., comparable values of τ_0, x, and Δh^*, the difference between T_g and T_a is especially critical. Whether this is the case for P2VP and PS or not, the difference of 6 deg between the respective T_g values is very important, since aging takes place at a single fixed aging temperature. The effective aging time t_{eff} for P2VP is therefore expected to be much longer than for PS. Consequently a reduction of the difference between the T_{max}s compared to the difference between the T_gs is not unlikely and, as described before, also observed experimentally.

This analysis suggests that the observation of two clearly separated enthalpy recovery peaks is indeed restricted to blends of very different components like PVC and PiPMA described in ref 1. Even if this conclusion would be true, the enthalpy recovery method will, as demonstrated, still work provided the position of the onset of the peaks as a function of log t_a is also taken into account. However, the real situation is more favorable. The linear relationship between T_{max} and log t_a for a given T_a is only valid as long as the system is still far from equilibrium. If equilibrium is approached, T_{max} becomes independent of t_a. Therefore at some value of T_a above 80 °C P2VP will be close to equilibrium already after a relatively short aging time, whereas PS will still be far away from equilibrium. In that case T_{max} of P2VP remains at a fixed position and T_{max} of PS will continue to increase linearly with log t_a. A first indication of this possibility was already found for the onset data discussed before. Experimentally this kind of situation is found for P2VP and PS for aging temperatures around 90 °C. Figures 7 and 8 show the thermograms of P2VP and PS, respectively, aged at 91 °C for the amounts of time indicated. For $t_a \geq 1$ h the position of T_{max} of P2VP is nearly independent of the aging time. The fact that P2VP is, after 1 h aging at 91 °C, close to equilibrium is confirmed by looking at the amount of enthalpy ΔH recovered as a function of the aging time. ΔH is also approximately independent of t_a. The position of the enthalpy recovery peak of PS continues to increase linearly with log t_a. It is found at 115 °C for $t_a = 1$ h, compared to 110 °C for P2VP, and shifts to 118 °C at larger times. Hence, after aging for 1 h the difference is already 5 °C and increases to 8 °C or more. Figure 9 shows the thermograms of P2VP–PS blends also aged at 91 °C for the amounts of time indicated. In the light of the foregoing discussion it comes as no surprise that already after a relatively short aging period two separated peaks become visible. Hence, a few hours of aging is sufficient to conclude that mixtures of P2VP and PS exposed for 5 min to 140 °C have a two-phase morphology. Figure 10 shows the position of the enthalpy recovery peaks of P2VP, PS, and blends of P2VP and PS as a function of log t_a. As in the case of phase-separated blends of PVC and PiPMA,[1] the positions of the two peaks of the blends virtually coincide with the corresponding peaks of the pure components. Furthermore, the onset of the enthalpy recovery peaks of P2VP and P2VP–PS blends are presented in Figure 10. The difference between these data is also relatively small, although as in the previous case of aging at T_a = 80 °C, the onset values of pure P2VP are slightly lower than the corresponding data for the blend. As stated before, these small but systematic differences probably

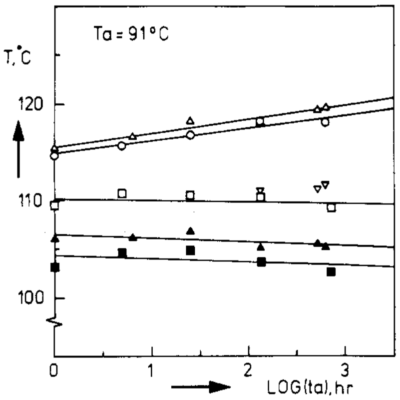

Figure 10. T_{max}, T_{ons} versus log t_a for P2VP, PS, and P2VP/PS: (○, □) T_{max} of PS and P2VP, respectively; (▽, △) first and second T_{max} of P2VP/PS, respectively; (■, ▲) T_{ons} of P2VP and P2VP/PS, respectively.

imply that both phases, but in particular the P2VP-rich phase, consist of a mixture of the two polymers. A peculiar feature of the experimental results is the fact that there is a slight tendency of the onset temperatures to fall off as a function of log t_a. So far, we have not found a theoretical or experimental explanation for this observation.

Because the difference in the glass transition temperatures is approximately 6 deg, there is another possible way of demonstrating the two-phase morphology of P2VP/PS blends. Annealing at 100 °C, close to the glass transition temperature of P2VP, will result in enthalpy relaxation of the PS-rich phase only. The DSC scan could in principle show a specific heat jump attributed to the P2VP-rich phase and an enthalpy recovery peak belonging to the PS-rich phase. In practice, because PS reaches equilibrium in a very short period, the endothermic peak virtually coincides with the specific heat jump of P2VP. Consequently, the two-phase morphology can be demonstrated most convincingly by aging around 90 °C.

Before any definite conclusion concerning the miscibility of two polymers is made, it is useful to look at the morphology of the blend as prepared, i.e., before any additional thermal treatment has been given. In our case the blends are obtained by adding a solution of the two polymers in a common solvent to an excess of a nonsolvent. After precipitation and evaporation of the low molecular components, a blend is obtained which at least in theory could be homogeneous or inhomogeneous, irrespective of the (im)miscibility of both polymers in the melt state. If an inhomogeneous blend is obtained, whereas the polymers actually are miscible in the melt state, annealing at some temperature above both glass transition temperatures for 5 min only may not be enough to rehomogenize the highly viscous system completely. The opposite case of a homogeneous blend of immiscible polymers will in general not pose any real problems. Annealing for 5 min in the melt not too close to the glass transition temperatures will almost certainly lead to local phase separation with domain sizes large enough to demonstrate the two phase morphology by either the single composition dependent T_g criterion or the enthalpy recovery method.

To demonstrate the usefulness of the enthalpy recovery method in relation to these questions, blends of P2VP and PS as obtained by coprecipitation and drying were also investigated. Figure 11 shows thermograms of these blends aged at 91 °C and not preexposed to temperatures above 50 °C except for the short time involved in bringing the blend to 91 °C. The shape of the enthalpy recovery peaks clearly indicate a two-phase morphology. In contrast to blends annealed at 140 °C for 5 min, a development of two very distinct endothermic peaks does not occur within the limited time span used. From this we could conclude that annealing for 5 min at 140 °C leads to a better defined two-phase morphology and hence that both polymers are indeed immiscible at 140 °C. However, this conclusion is not really justified since the enthalpy relaxation process is strongly related to the distribution of free volume in the samples, which will be completely different for the two situations considered. In general, additional experiments using longer annealing times in the melt state should be performed before any definite conclusion is drawn. In our case, this is unnecessary, since the immiscibility of P2VP and PS in the melt state is well-known from recent studies of styrene and 2-vinylpyridine block copolymers.[33-35]

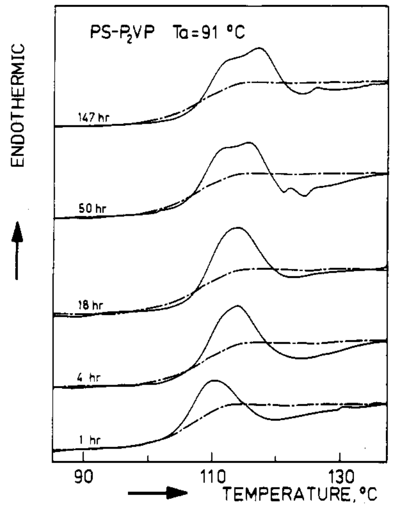

Figure 11. Thermograms of P2VP/PS aged at 91 °C for the times indicated and not preexposed to temperatures above 50 °C: first scan (—); second scan (- - -).

Concluding Remarks

The enthalpy recovery method has been applied to a number of polymer blends now and several conclusions can be drawn. Based on our investigations it is believed to be a valid experimental technique to establish polymer blend phase behavior in all cases where the glass transition temperatures of the pure components are too close to each other to use the conventional single compositional dependent T_g criterion. Even if the T_gs of the pure components are sufficiently far apart to distinguish between the relevant discontinuities of specific heat it may be a useful alternative since several observations suggest that it is a very sensitive method. In this respect we think of block copolymer systems with characteristic mesomorphic structures. Another example could be very small sample sizes. This enhanced sensitivity is the subject of our ongoing research program.

The relevant parameter for the enthalpy recovery method is the effective aging time t_{eff} defined by eq 5 and 7. If both components have nearly identical T_gs, t_{eff} will in general still be different due to differences in the material constants A, Δh^*, x, and β. In that case the appropriate aging temperature will be given by $T_a \simeq T_g - 20$, since for a given aging time the peak height is calculated to pass through a maximum at this temperature.[20] This corresponds precisely to the conditions employed in our investigation of the PVC/PiPMA blends.[1] If the T_gs are somewhat more apart, as is the case for P2VP and PS, it may be more appropriate to chose the aging temperature relatively close to the T_g of the pure component with the lowest glass transition temperature. In that case the difference between the positions of the maxima of the enthalpy recovery peaks of the pure components increases as a function of aging time since the component with the lowest T_g approaches equilibrium after a short aging time.

Finally, it is important to realize that multiple enthalpy recovery peaks may also occur in pure polymer systems.[31] Therefore, conclusions concerning phase behavior of polymer blends based on the enthalpy recovery method always require a comparison between the enthalpy recovery behavior of the blend and of the pure components.

Acknowledgment. It is a pleasure to acknowledge Y. Y. Tan for his suggestion to apply the enthalpy recovery method to the P2VP/PS system.

Registry No. PS, 9003-53-6; P2VP, 25014-15-7.

References and Notes

(1) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(2) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(3) Ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(4) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(5) Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763.
(6) Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1987**, *27*, 1482.
(7) Olabishi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.
(8) Hodge, I. M.; Berens, A. R. *Macromolecules* **1982**, *15*, 762.
(9) DeBolt, M. A.; Easteal, A. J.; Macedo, P. B.; Moynihan, C. T. *J. Am. Ceram. Soc.* **1976**, *59*, 16.
(10) Moynihan, C. T.; et. al. *Ann. N. Y. Acad Sci.* **1976**, *279*, 15.
(11) Kovacs, A. J.; Aklonis, J. J.; Hutchinson, J. M.; Ramos, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1079.
(12) Nagi, K. L. *Comments Solid State Phys.* **1979**, *9*, 127; **1980**, *9*, 141.
(13) Robertson, R. E.; Simha, R.; Curro, J. G. *Macromolecules* **1984**, *17*, 911.
(14) *Relaxations in Complex Systems*; Ngai, K. L., Wright, G. B., Eds.; U.S. Government Printing Office: Washington, DC, 1985. (Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.)
(15) McKenna, G. B. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon Press: Oxford, 1988; Vol. 2, Properties.
(16) Rendell, R. W.; Ngai, K. L.; Fong, G. R.; Aklonis, J. J. *Macromolecules* **1987**, *20*, 1070.
(17) Tool, A. Q. *J. Am. Ceram. Soc.* **1946**, *29*, 240.
(18) Gardon, R.; Narayanaswamy *J. Am. Ceram. Soc.* **1970**, *53*, 148.
(19) Narayanaswamy *J. Am. Ceram. Soc.* **1971**, *54*, 491.
(20) Hodge, I. M. In ref 14, p 65.
(21) Margaritis, A. G.; Kallitsis, J. K.; Kalfoglou, N. K. *Polymer* **1987**, *22*, 2122.
(22) Cowie, J. M. G.; Lath, D. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 103.
(23) Illers, K. H. *Makromol. Chem.* **1969**, *127*, 1.
(24) Gray, A.; Gilbert, M. *Polymer* **1976**, *17*, 44.
(25) Berens, A. R.; Hodge, I. M. *Macromolecules* **1982**, *15*, 756.
(26) Kovacs, A. J. *Fortschr. Hochpolym. Forsch.* **1963**, *3*, 394.
(27) Shaw, M. T. *J. Appl. Polym. Sci.* **1974**, *18*, 449.
(28) Hodge, I. M.; Huvard, G. S. *Macromolecules* **1983**, *16*, 371.
(29) Privalko, V. P.; Demchenko, S. S.; Lipatov, Y. S. *Macromolecules* **1986**, *19*, 901.
(30) Hodge, I. M.; Berens, A. R. *Macromolecules* **1981**, *14*, 1599.
(31) Ruddy, M.; Hutchinson, J. M. *Polym. Commun.* **1988**, *29*, 132.
(32) Ellis, T. S.; Karasz, F. E. *Polym. Eng. Sci.* **1986**, *26*, 290.
(33) Matsushita, Y.; Nakao, Y.; Saguchi, R.; Choshi, H.; Nagasawa, M. *Polym. J. (Tokyo)* **1986**, *18*, 493.
(34) Hadziioannou, G., private communications.
(35) Creton, C.; Kramer, E. J.; Hadziioannou, G. *Bull. Am. Phys. Soc.* **1988**, *33*, 586.

Clearing Temperatures of Aramid Solutions in Sulfuric Acid

S. J. Picken*

Akzo Research, Corporate Research Department, Arnhem, Postbox 9300,
6800 SB ARNHEM, The Netherlands.
Received July 25, 1988;
Revised Manuscript Received September 27, 1988

ABSTRACT: Measurements of the nematic–isotropic transition temperatures of solutions of poly(*p*-phenyleneterephthalamide), poly(*p*-benzamide), and poly(4,4′-benzanilidyleneterephthalamide) in concentrated sulfuric acid are presented as a function of concentration and average molecular weight. The results indicate a strong influence of molecular flexibility on the clearing temperature. The experiments are explained by a mean-field theory analogous to the Maier–Saupe theory for low molecular weight nematic liquid crystals.

Introduction

In this paper measurements of the nematic–isotropic transition (or clearing) temperatures of solutions of PPTA (poly(*p*-phenyleneterephthalamide)) and other aramids in concentrated H_2SO_4 are presented. The results show a marked influence of polymer concentration on the clearing temperature. The slope of the concentration–clearing temperature graphs depends on the average molecular weight of the polymer. This indicates a coupling of the (temperature dependent) molecular flexibility to the phase transition.

Molecular flexibility is usually described by the so-called persistence length. An influence of temperature on the persistence length has been found experimentally for a variety of materials, e.g., (acetoxypropyl)cellulose[1] and can also be derived theoretically from a wormlike model for polymer chains (see Appendix).

Basically two mechanisms can lead to formation of a nematic phase: the first is dealt with in the traditional Onsager or Flory type of approach.[2,3] This shows that, depending on the axial ratio of the rodlike particles, there is a critical concentration above which a nematic phase is formed. This concentration does not depend on the temperature of the system as these theories are essentially athermal; i.e., the part of the free energy that leads to the anisotropy is an entropy term.

A later version of the Flory theory describes a system of semiflexible particles. The persistence length is used to determine an effective axial ratio for the particles.[4] A temperature-dependent persistence length thus leads to a "thermotropic" type of behavior where the phase transition is governed by the temperature as well as the concentration.

An alternative mechanism is used by the Maier-Saupe mean field theory.[5] Here the stability of the nematic phase is explained from an anisotropic potential. Despite the complete neglect of the excluded-volume (entropy) terms in the free energy, the temperature dependence of the $\langle P_2 \rangle$

0024-9297/89/2222-1766$01.50/0