du CNRS, 15, quai Anatole France 75007 Paris; p 82.
(17) de Gennes, P. G. *Macromolecules* **1976**, *9*, 587, 594. See also ref 8.
(18) See, for instance, ref 8, pp 211–2.
(19) See: Dejardin, P.; Varoqui, R. *J. Chem. Phys.* **1981**, *75*, 4115.
(20) To make contact with the classical literature in this field, it is instructive to write down the full equation of $\psi(z)$ obtained by minimization of eq I.13. Consider, for instance, the noninteracting case where G reduces to a classical potential term $(-\mu\psi^2)$. Then ψ (and the concentration ψ_2) has the exponential form discussed by Hoeve, Rubin, and others: see ref 4 for a review of these aspects.
(21) It has been pointed out to us by E. A. DiMarzio that if the surface is heterogeneous and has only a few spots of strong attraction (possibly related to steps or dislocations on the solid), one expects that Γ does increase with M.

Miscibility of the Poly(hydroxy ether) of Bisphenol A with Water-Soluble Polyethers

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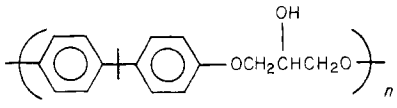
ABSTRACT: The miscibility of the poly(hydroxy ether) of bisphenol A (phenoxy) with the water-soluble polyethers poly(ethylene oxide) and poly(vinyl methyl ether) has been established by using dynamic mechanical methods. The observed miscibility is proposed to be the result of specific interactions between the pendant hydroxyl of phenoxy (proton donor) and the ether group of the respective polyethers (proton acceptor). Poly(propylene oxide) and poly(vinyl ethyl ether) are both water insoluble and do not exhibit miscibility with phenoxy, presumably due to poorer hydrogen-bonding capabilities for these polyethers (as evidenced by the water insolubility). The addition of phenoxy to poly(ethylene oxide) significantly lowers the crystallization rate, as expected, due to a T_g increase. This allows the preparation of amorphous specimens and, thus, the extrapolation of T_g–composition data to determine the T_g of amorphous poly(ethylene oxide) (–73 °C). A significant T_g increase occurs with the crystallization of poly(ethylene oxide) from blends with phenoxy due to an increase in the amorphous phase concentration of phenoxy and chain stiffening due to the presence of spherulitic structure. From the T_g shift and a simple material balance, the degree of crystallinity and $\Delta H_f°$ of poly(ethylene oxide) can be directly calculated. These data were used to calculate a degree of crystallinity of 70% for the unblended poly(ethylene oxide), in excellent agreement with previously reported data obtained by more classical techniques.

Introduction

In the past decade, many examples of miscible polymer pairs have been cited in the technical literature,[1] indicating that preparation of miscible polymer systems was more feasible than previously believed.[2] Many of the recently reported miscible systems are believed to achieve miscibility via specific interactions (e.g., hydrogen bonding). Phenoxy, the poly(hydroxy ether) of bisphenol A, offers



phenoxy

excellent potential for hydrogen bonding as a proton donor because of its pendant hydroxyl. Phenoxy has been previously shown to exhibit miscibility with poly(ε-caprolactone),[3] poly(butylene terephthalate),[4] a cyclohexanedimethanol-based polyester,[4] a polyester-based polyurethane,[5] poly(ethylene adipate),[6] and poly(butylene adipate).

Poly(ethylene oxide), a water-soluble polymer, exhibits miscibility with poly(acrylic acid),[7] poly(methacrylic acid),[8] a vinyl methyl ether/maleic anhydride copolymer,[9] (carboxymethyl)cellulose sodium salt,[9] and (carboxymethyl)dextran.[9] These miscible blends exhibit particularly strong specific interactions and thus are generally referred to as complexes. Although the above-mentioned poly(ethylene oxide) blends are with other water-soluble polymers, at neutral or low pH a precipitate is immediately formed when water solutions of the respective constituents are mixed. Other samples of complexation involving poly(ethylene oxide) include blends with polyureas and phenolics.[9] Poly(ethylene oxide) acts as the proton acceptor in the hydrogen-bonding interactions with these polymers.

With this background, phenoxy/poly(ethylene oxide) blends have an excellent potential for hydrogen-bonding interactions and therefore the phase behavior of their blends would be expected to be quite interesting. Indeed this is the case, and miscibility over the entire composition range was observed and is the subject of this paper.

Another water-soluble polyether, poly(vinyl methyl ether) (PVME), is expected to interact as a proton acceptor in blends with proton-donor polymers. Blends of PVME with phenoxy are also miscible over the entire composition range, as will be illustrated by the data reported in this paper. PVME/polystyrene blends have been reported as miscible in various investigations[10–12] and are particularly studied in regard to the observed lower critical solution temperature (LCST) behavior.[10,11,13] Phenoxy/PVME blends interestingly also exhibit LCST behavior. Lower critical solution temperature behavior, in which phase separation occurs with increasing temperature, is typical for mixtures of high molecular weight polymers.

Experimental Section

Blends of phenoxy (PKHH, Union Carbide Corp.; reduced viscosity = 0.43 dL/g measured as 0.2 g/100 mL in tetrahydrofuran at 25 °C) and poly(ethylene oxide) (WSR-301, Union Carbide Corp.; molecular weight approximately 4 000 000) were prepared in a brabender at 175–190 °C for 8–10 min. The resultant mixtures were then compression molded into 30-mil thick samples at 160–180 °C. Except where specifically designated, the samples were stored in a vacuum desiccator until testing. Dynamic mechanical measurements were made with a torsion pendulum

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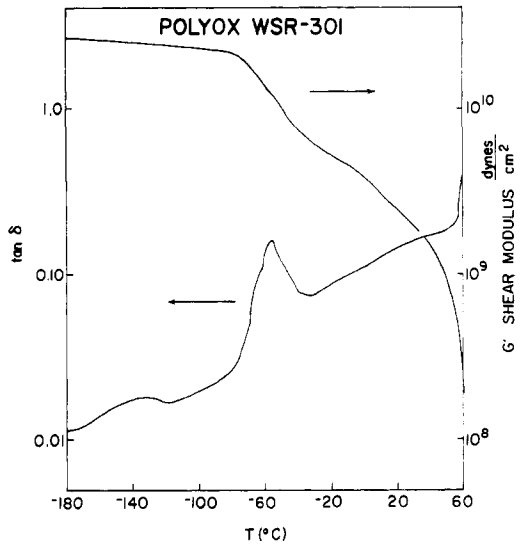

Figure 1. Dynamic mechanical results on poly(ethylene oxide) Polyox WSR-301.

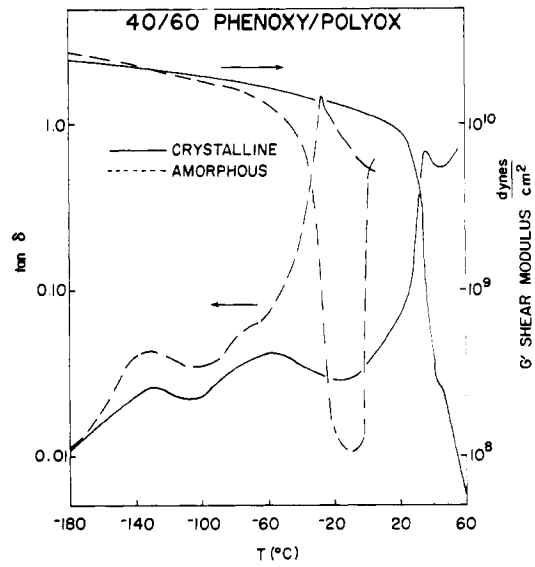

Figure 2. Dynamic mechanical results on 40/60 (by weight) phenoxy/Polyox blend.

similar to a design reported by Neilsen.[14] Crystallization rate studies were also conducted with a torsion pendulum. Calorimetric data were obtained with a differential scanning calorimeter (Perkin-Elmer DSC-2). The melting point, T_m, for unblended poly(ethylene oxide) and in the blends with phenoxy was determined from the peak of the melting endotherm, and the heat of fusion, ΔH_f, was determined from the area under the melting endotherm. The time required to reach the peak of the crystallization exotherm, t_c, at 25 °C was determined on the above-cited blends after heating to 100 °C followed by rapid cooling (~160 °C/min) to 25 °C.

Phenoxy/PVME blends were also prepared by melt mixing in a brabender at 150–180 °C. The PVME utilized was Gantrez M-556 (GAF Corp.) and was devolatilized prior to melt blending to remove the solvent (toluene) in the as-received sample.

With a procedure quite similar to that previously reported in crystallization rate studies with poly(ϵ-caprolactone) from poly(ϵ-caprolactone)/poly(vinyl chloride) blends,[15] the crystallization rate for poly(ethylene oxide) in blends with phenoxy was determined from shear modulus–time measurements by means of a torsion pendulum. Samples were heated between two platens of a compression-molding press to 100 °C and then rapidly cooled to room temperature. The sample was then placed between the grips of a torsion pendulum and the time-modulus measurements were taken.

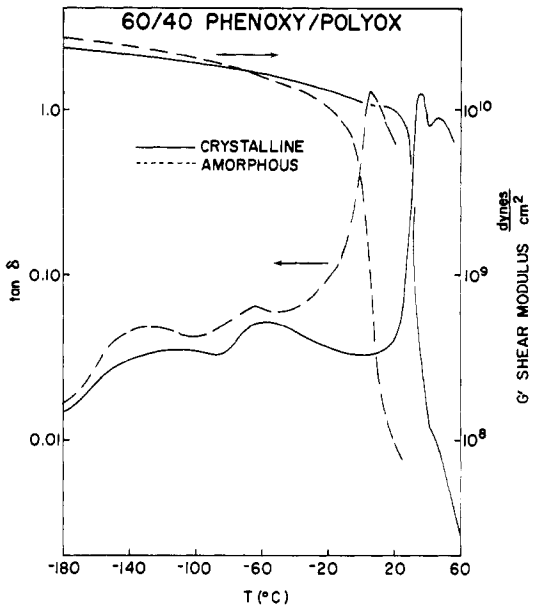

Figure 3. Dynamic mechanical results on 60/40 (by weight) phenoxy/Polyox blend.

Table I
Calorimetric and Dynamic Mechanical Results on Phenoxy/Poly(ethylene oxide) Blends

wt % PEO	T_m, °C	ΔH_f(blend), cal/g	t_c at 25 °C, s	T_g, °C amorphous	T_g, °C crystalline
100	67	30.3	58		−57
85	63	27.5	92		10
75	60	24.0	97	−47	20
65	59	21.0	179	−37	34
60	61	19.4	246	−27	36
55	58	17.8	504	−25	43
50	60	15.8	918	−16	45
45	58	13.7		−5	43
40	56	10.5		6	40
35	56	9.4		15	39
30	amorphous			24	
20	amorphous			46	
10	amorphous			66	
0	amorphous			96	

Experimental Results. The dynamic mechanical results (tan δ, mechanical loss; G', shear modulus) (nominal frequency of 1 Hz in the glassy state) for phenoxy PKHH have been reported previously.[4] The results for poly(ethylene oxide) WSR-301 are shown in Figure 1, illustrating a T_g of −57 °C and a melting point around 65 °C. Similar data for 40/60 and 60/40 (by weight) phenoxy/poly(ethylene oxide) blends are illustrated in Figures 2 and 3. The blends exhibit a single, sharp glass transition temperature intermediate between the constituent values for the amorphous samples, which were heated above the melting point and rapidly quenched to liquid nitrogen temperatures, and the crystalline samples, which were annealed at 23 °C for 1 month in a vacuum desiccator. A large increase in the T_g accompanied by a decrease in the tan δ peak height occurs with crystallization for the blends rich in poly(ethylene oxide).

The calorimetric results are listed in Table I along with the T_g data for the various blends determined from dynamic mechanical experiments. At and above 70 wt % phenoxy, no crystalline endotherm was observed, and above 50 wt % phenoxy, the crystallization rate at 25 °C was too slow to determine the time to reach the maximum crystallization rate, t_c, via the calorimetric method.

The crystallization rate determined by the dynamic mechanical technique is illustrated in Figure 4 for a series of phenoxy/poly(ethylene oxide) blends. The results clearly illustrate the effect of increasing phenoxy concentration on the lowering of the poly(ethylene oxide) crystallization rate, as expected for the ad-

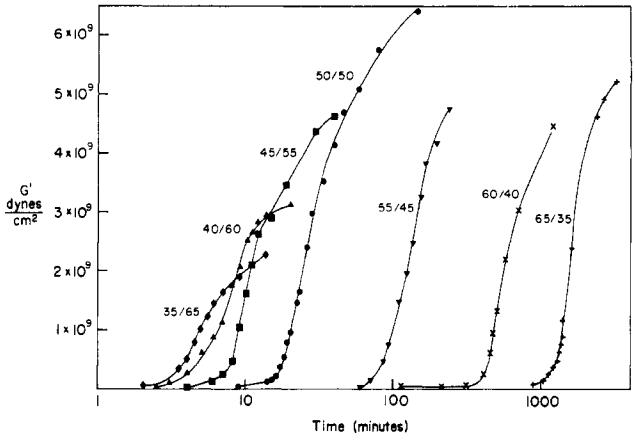

Figure 4. Shear modulus vs. time for various phenoxy/poly(ethylene oxide) blends (amorphous at $t = 0$).

Table II
Water Immersion Results on Phenoxy/Polyox Blends

composition phenoxy PKHH/ Polyox WSR-301	% water content[a]	% extractables
60/40	60.5	12.5
50/50	109	19.1
40/60	187	25.6
25/75	330	59.1

[a] One month immersion; percent based on final dry weight.

dition of a higher T_g miscible polymer to a crystalline polymer.

As poly(ethylene oxide) is water soluble, the sorption and water extraction data for the blends should be interesting. Samples of 30-mil thickness were immersed in distilled water (with measurements taken and water changed weekly). At high poly(ethylene oxide) levels, a peak in sorption was observed followed by a slow decrease due to poly(ethylene oxide) extraction. The results at the end of 1 month are listed in Table II.

The dynamic mechanical results on 50/50 and 25/75 phenoxy/PVME blends are illustrated in Figure 5.

Discussion and Analysis of Experimental Results

The dynamic mechanical results clearly illustrate the miscibility of phenoxy and poly(ethylene oxide). A plot of the T_g vs. composition data (listed in Table I) is illustrated in Figure 6. The amorphous blend T_g data reasonably fit the Fox equation

$$1/T_g = W_a/T_{g_a} + W_b/T_{g_b} \quad (1)$$

where T_{g_a}(phenoxy) = 369 K, T_{g_b}[poly(ethylene oxide)] = 200 K, and W_i = weight fraction. Note that the T_g assigned to poly(ethylene oxide) is an extrapolated value. Using the experimental technique (previously mentioned) for quenching does not yield amorphous poly(ethylene oxide), as the crystallization rate is more rapid than the cooling rate. A literature search did not reveal an experimentally determined T_g value for poly(ethylene oxide), and a recent review of poly(ethylene oxide)[16] properties only cites values obtained on crystalline samples. The miscible blend extrapolation approach utilized here allows for a facile method for the determination of the amorphous T_g for rapidly crystallizable polymers. This technique has been previously demonstrated for the amorphous T_g determination of poly(ϵ-caprolactone) by extrapolation of T_g data of poly(ϵ-caprolactone)/poly(vinyl chloride) mixtures.[17]

The crystallization kinetics of a crystalline polymer blended with another miscible polymer (particularly with a significant difference in the constituent T_g values) will

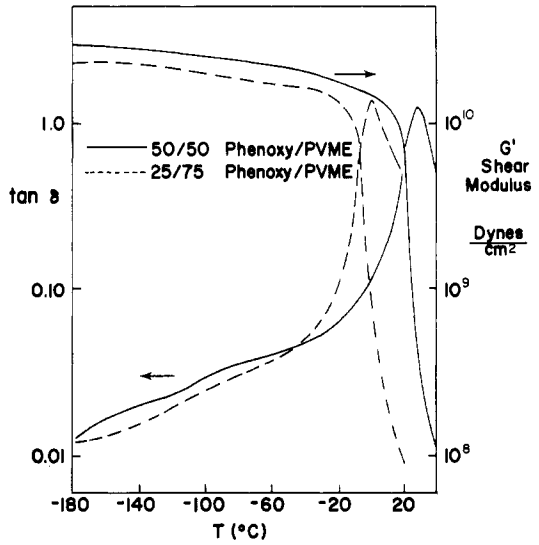

Figure 5. Dynamic mechanical results on 50/50 and 25/75 (by weight) phenoxy/poly(vinyl methyl ether) blends.

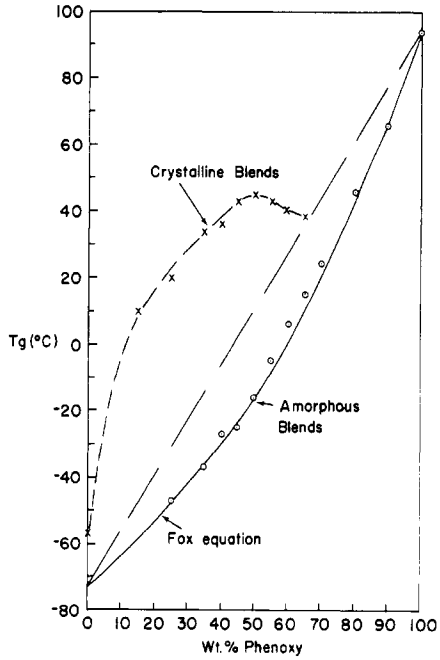

Figure 6. T_g vs. composition data for phenoxy/poly(ethylene oxide) blends.

be expected to be different from those in the unblended state. The difference in crystallization rate is primarily due to the chain mobility change due to a variation in the T_g. Other factors do contribute to a kinetic difference, including a dilution effect and a potential change in the equilibrium melting point, $T_m°$. Cases of increased crystallization kinetics where the T_g of the crystallizable polymer decreases with added miscible polymer include bisphenol A polycarbonate crystallization from blends with poly(ϵ-caprolactone).[18]

With the T_g of phenoxy significantly higher than that of poly(ethylene oxide), a significant decrease in crystallization rate is observed with increasing phenoxy concentration. Prior studies with poly(ϵ-caprolactone) crystallization from blends with poly(vinyl chloride) had shown good agreement when the data were analyzed with the spherulite growth rate equation[19]

$$G = G_0 \exp(-\Delta F^*/RT) \exp[-4b_0\sigma\sigma_e T_m°/\Delta H_f(\Delta T)kT] \quad (2)$$

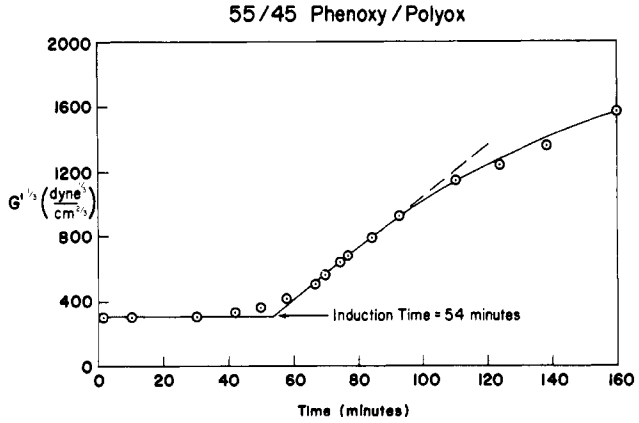

Figure 7. $G^{4/3}$ [(shear modulus)$^{1/3}$] vs. time for 55/45 phenoxy/Polyox blend (amorphous at $t = 0$).

where ΔF^* represents the barrier restricting polymer chain diffusion to the crystallizing surface, b_0 the monolayer thickness, σ the lateral interfacial free energy, σ_e the interfacial free energy of the chain-folded surface, T_m° the equilibrium melting point, ΔH_f the heat of fusion, ΔT the difference $T - T_m$, and G the radial growth rate (dr/dt) of the spherulite. ΔF^* has been considered by Hoffman and Weeks[20] to be satisfied by the William, Landel, and Ferry (WLF) equation:[21]

$$\Delta F^* = 4120T/(51.6 + T - T_g) \quad (3)$$

As the modulus of an amorphous specimen ($T_g <$ test temperature) is assumed to be proportional to the volume fraction of spherulites, the following method may be employed to analyze modulus–time data in a form proportional to $G(dr/dt)$:

$$G' = \tfrac{4}{3}\pi r^3 k \quad \text{(note } G' = \text{shear modulus)} \quad (4)$$

$$\frac{dG^{4/3}}{dt} = (\tfrac{4}{3}\pi k)^{1/3}\frac{dr}{dt} \quad (5)$$

$$\frac{dG^{4/3}}{dt} = k'(1 - W_d)\exp\left(-\frac{4120}{(51.6 + T - T_g)R}\right) \quad (6)$$

$$k' = (\tfrac{4}{3}\pi k)^{1/3}G_0\exp\left(-\frac{4b_0\sigma\sigma_e T_m^\circ}{\Delta H_f(\Delta T)kT}\right) \quad (7)$$

The values of b_0, σ, σ_e, T_m°, and ΔH_f were assumed constant as previously with PCL/PVC blends. As T_m will vary with composition due to melting point depression (and possibly T_m°), some error will be present; however, as the data previously presented indicate, this is quite small relative to the major change in crystallization rate due to the T_g change. Note the term $1 - W_d$ is included to correct for the dilution in concentration by incorporation of an amorphous diluent.

From the linear portion of a plot of $G^{4/3}$ vs. time, values of $dG^{4/3}/dt$ were obtained as shown in Figure 7. The $dG^{4/3}/dt$ data are illustrated in Figure 8 as a function of composition and are listed in Table III along with the induction time for crystallization. In Figure 8, the calculated predictions of eq 6 are shown, with k' calculated from the experimental data at the intermediate concentration. Unlike the previously reported PCL/PVC system,[15] poor agreement of the experimental with the predicted crystallization rate is observed.

The glass transition temperature of the phenoxy/poly(ethylene oxide) blend increases significantly with crystallization of poly(ethylene oxide), due primarily to the increase in phenoxy concentration in the residual amorphous phase. An additional increase in T_g is due to the stiffening of the amorphous phase by the reinforcement of poly(ethylene oxide) spherulites. As the phenoxy concentration in the residual amorphous phase can be determined from the resultant T_g of the crystallized sample, a simple material balance can be utilized to determine the degree of crystallinity of poly(ethylene oxide) in the sample. With calorimetric measurements of ΔH_f, the degree of crystallinity of unblended poly(ethylene oxide) can likewise be determined as well as ΔH_f° for poly(ethylene oxide). This approach has been successfully applied to poly(ε-caprolactone) by analysis of a material balance for poly(ε-caprolactone/poly(vinyl chloride) mixtures.[22]

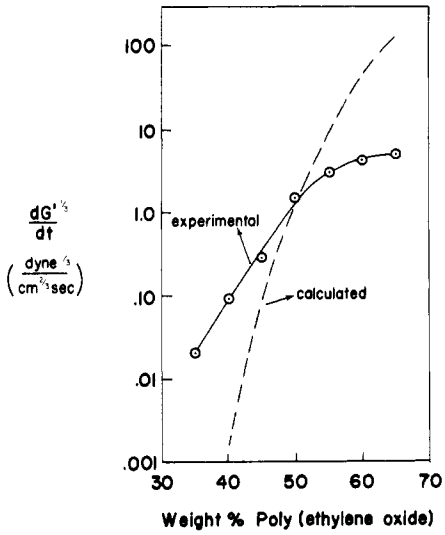

Figure 8. Crystallization rate of poly(ethylene oxide) as a function of poly(ethylene oxide) concentration.

Table III
Crystallization Rate Data

wt % PEO	induction time, min	$dG'^{1/3}/dt$, dyn$^{1/3}$/(cm$^{2/3}$ s) exptl	calcd[a]
65	1.8	4.48	130.3
60	2.5	4.02	22.9
55	5.3	3.15	13.9
50	13.5	1.61	1.6
45	54	0.278	0.61
40	351	0.0915	0.0013
35	922	0.0228	0.000013

[a] Calculated with $k' = 2.78 \times 10^{10}$; k' calculated at center of experimental data (50% poly(ethylene oxide)).

For the determination of the degree of crystallinity of poly(ethylene oxide) in crystallized blends of phenoxy/poly(ethylene oxide), the following material balance was employed:

$$W_{PEO} = W_{aPEO}X_a + X_c \quad (8)$$

where W_{PEO} is the weight fraction of poly(ethylene oxide) in the blend, W_{aPEO} is the weight fraction of poly(ethylene oxide) in the residual amorphous phase of the crystalline blend, X_a is the weight fraction of the amorphous phase, and X_c is the weight fraction of the crystalline phase (pure poly(ethylene oxide)). As $X_a + X_c = 1.0$, eq 8 reduces to

$$X_c = W_{PEO} - W_{aPEO}(1 - X_c) \quad (9)$$

From T_g vs. composition data, W_{aPEO} can be determined after an appropriate correction is made for the T_g shift resulting from poly(ethylene oxide) crystallization. The experimentally observed T_g, $\Delta T_{g\,exptl}$, is set equal to

$$\Delta T_{g\,exptl} = \Delta T_{gc} + \Delta T_{gs} \quad (10)$$

Table IV
Degree of Crystallinity Calculations

phenoxy/Polyox ratio	T_{g_a}, °C	T_{g_c}, °C	ΔH_f, cal/g	W_a(Polyox)	X_c	X_c',[a] %	$\Delta H_f°$,[b] cal/g
25/75	−47	19	24.0	0.39	0.590	78.7	40.7
35/65	−37	34	21.0	0.29	0.507	78.0	41.4
40/60	−27	36	19.4	0.275	0.448	74.7	43.3
45/55	−25	43	17.8	0.24	0.408	74.3	42.4
50/50	−16	45	15.8	0.22	0.359	71.8	44.0
55/45	−5	43	13.7	0.225	0.303	67.3	45.2
60/40	6	40	10.5	0.225	0.226	56.5	46.4
65/35	15	39	9.4	0.230	0.156	44.6	[c]
0/100	−73	57	30.3	0.300	0.700	70.0	

[a] X_c' is the degree of crystallinity of poly(ethylene oxide) in the blend. [b] Average $\Delta H_f°$ for blends = 43.3 cal/g. [c] 60.3 cal/g (not used for calculating average ΔH_f).

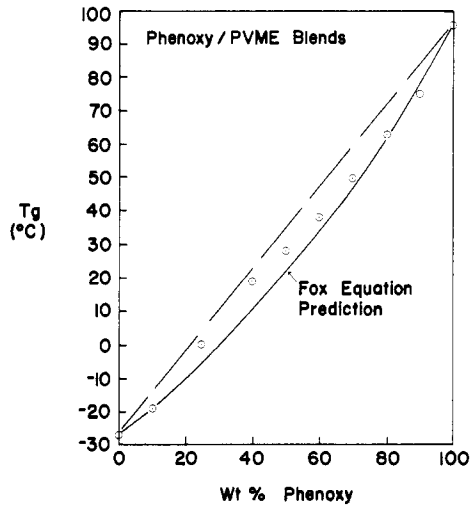

Figure 9. T_g vs. composition data for phenoxy/poly(vinyl methyl ether) blends.

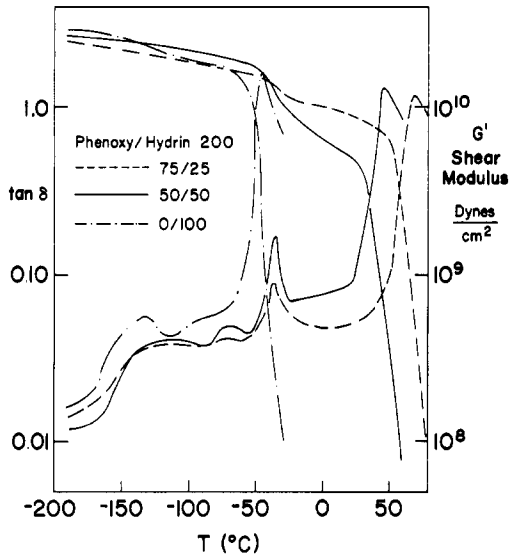

Figure 10. Dynamic mechanical results on phenoxy/epichlorohydrin–ethylene oxide copolymer (Hydrin 200) blends.

where ΔT_{gc} is the T_g shift for a composition change in the amorphous phase due to crystallization of poly(ethylene oxide) and ΔT_{gs} is equal to the T_g change due to stiffening of the residual amorphous phase by spherulitic reinforcement. ΔT_{gs} can be calculated from the degree of crystallinity of the blend divided by the degree of crystallinity of the unblended poly(ethylene oxide) times the T_g shift for poly(ethylene oxide) due to crystallization (−73 to −57 °C). That is

$$T_{gs} = \frac{\Delta H_f(\text{blend})}{\Delta H_{f\,PEO}(\text{unblended})} \times 16\ °C \qquad (11)$$

Thus, ΔT_{gc} can be calculated and used to determine the poly(ethylene oxide) content of the residual amorphous phase by utilizing the T_g vs. composition data illustrated in Figure 6.

Using this approach, we calculated the degree of crystallinity for a series of blends as well as $\Delta H_f°$ for poly(ethylene oxide) (Table IV). From the ΔH_f of unblended poly(ethylene oxide) a degree of crystallinity of 70% was calculated. This compares favorably with literature values of 69–73% for unstabilized poly(ethylene oxide) of similar molecular weight determined from X-ray diffraction data.[23]

The T_g vs. composition data for the phenoxy/PVME blends are shown in Figure 9 and compared with predictions of the Fox equation. All blends exhibited a single T_g, indicating miscibility, although the transitional behavior of the blends was broader than for the unblended constituents.

As phenoxy exhibits miscibility with poly(ethylene oxide), blends with an ethylene oxide/epichlorohydrin copolymer (Hydrin 200) were made. The dynamic mechanical results (Figure 10) indicate phase separation exists; however, the phenoxy phase contains an appreciable amount of Hydrin 200 as evidenced by the decreasing T_g of the phenoxy-rich phase. The Hydrin-rich phase T_g is virtually unchanged by the presence of phenoxy. This result indicates the Hydrin 200 material may have compositional variations, with the ethylene oxide rich units exhibiting miscibility with phenoxy. Mixtures of phenoxy and poly(epichlorohydrin) were two-phase mixtures with no appreciable miscibility. Likewise, phenoxy and poly(propylene oxide) (Parel 58, Hercules) exhibited two-phase behavior. The next member of the poly(vinyl alkyl ether) family, namely, poly(vinyl ethyl ether), EDBM (Union Carbide Corp.), also exhibited two-phase behavior in phenoxy blends. It is interesting to point out that poly(propylene oxide) and poly(vinyl ethyl ether) are both water insoluble.

Discussion of Results

The water-soluble polyethers poly(ethylene oxide) and poly(vinyl methyl ether) exhibit miscibility with the poly(hydroxy ether) of bisphenol A as judged by the emergence of a single T_g for the respective blends intermediate between that of the constituents. The hydrogen-bonding capabilities of the above-mentioned polyethers are obviously reflected in their solubility in water, and this feature probably translates to the observed miscibility with phenoxy due to specific hydrogen-bonding

interactions. It is of interest to note that the next higher homologues of the polyethers (poly(propylene oxide) and poly(vinyl ethyl ether)) are not water soluble and are also not miscible with phenoxy.

The extrapolation of the T_g vs. composition data for amorphous phenoxy/poly(ethylene oxide) blends yields a T_g of −73 °C for poly(ethylene oxide). To our knowledge this is the first example of the reported T_g for amorphous poly(ethylene oxide). This result demonstrates the feasibility of the miscible polymer approach in experimentally determining the T_g of crystalline polymers as has been previously utilized for poly(ϵ-caprolactone) amorphous T_g determination.[17]

The crystallization rate of poly(ethylene oxide) is significantly lowered by the addition of phenoxy due to the increase in T_g and thus the reduction in chain mobility. The experimental crystallization rate vs. composition data obtained were in poor agreement with the prediction of the WLF equation functional dependence of the spherulitic growth rate equation. Prior data on the crystallization rate of PCL from PCL/PVC blends exhibited good agreement with the spherulitic growth rate equation prediction.[15]

The poor agreement with the T_g dependence of the spherulitic growth rate equation is not clearly understood; however, a number of possible reasons for this will be mentioned. The T_g of the blend is continuously changing once crystallization commences and the $dG^{1/3}/dt$ data (while determined at the initial linear slope early in the crystallization process) undoubtedly will be influenced by this change. The melting point is depressed by the addition of phenoxy (as well as the equilibrium melting point) and was not corrected for in the analysis. In the range of crystallization rate data (35–65 wt % poly(ethylene oxide)), the variation in T_m (Table I) is 5 °C. While this correction would make the analysis more exact, it is considered only a minor error and not the major reason for the disagreement of theory with experimental data. Less than ideal (random) mixing, leading to concentration fluctuations, may also be a factor. The poly(ethylene oxide) crystallization rate is presumably molecular weight dependent. As no thermal stabilizer was added, degradation of poly(ethylene oxide) to lower molecular weight may have occurred and thus would alter the results relative to a system in which the molecular weight was held constant. Note that a previous study[23] has established that the degradation of poly(ethylene oxide) is accompanied by an increase in the degree of crystallinity. Any variation in the interfacial free energy terms, σ and σ_e, would also influence the poor agreement between theory and experimental results.

A significant shift of the T_g for the poly(ethylene oxide)/phenoxy blends occurs with poly(ethylene oxide) crystallization due to a decrease in poly(ethylene oxide) in the amorphous phase as well as chain stiffening due to crystallization (which also increases the T_g of poly(ethylene oxide) over that observed in the amorphous state). By a simple material balance, the degree of crystallinity of poly(ethylene oxide) can be calculated from the T_g shift. This value combined with calorimetric data (heat of fusion) on unblended poly(ethylene oxide) can be utilized to calculate $\Delta H_f°$ and the degree of crystallinity for poly(ethylene oxide) (70%). This value is in good agreement with literature values reported for similar molecular weight poly(ethylene oxide).[23] The T_g shift approach for the determination of the degree of crystallinity of a crystalline polymer in a miscible blend appears to work quite well and the above example enhances this technique which was first demonstrated with poly(ϵ-caprolactone) in PCL/PVC blends.[22]

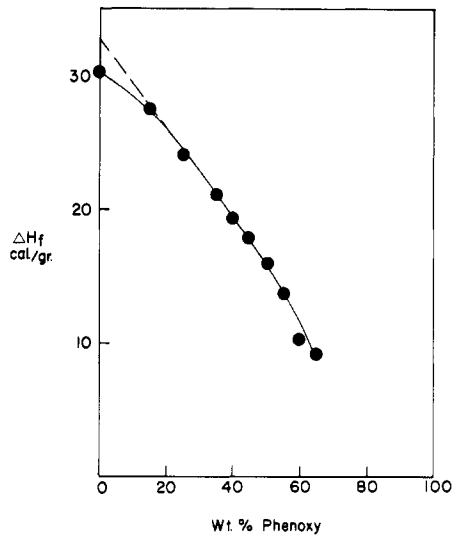

Figure 11. Heat of fusion of poly(ethylene oxide) in phenoxy/poly(ethylene oxide) blends.

Poly(ethylene oxide) in blends with phenoxy exhibits a higher degree of crystallinity (down to 45 wt % poly(ethylene oxide)) than unblended poly(ethylene oxide) (degree of crystallinity calculated on basis of poly(ethylene oxide) content of blends; see Table IV and Figure 11). This also has been observed with poly(butylene terephthalate) in blends with phenoxy,[4] where the ΔH_f data for the blends exhibited a maximum deviation from linearity. This observation is unexpected and no explanation can be offered at this time.

It is of interest to point out that while the initially amorphous samples were allowed to crystallize at 25 °C for 1 month, the T_g's of the resultant crystalline samples were in excess of 25 °C (as high as 45 °C). This would appear to indicate that crystallization occurred in the glassy state. However, the time scale of the T_g determination experiment (~1 Hz in the glassy state) yields a much higher frequency than for the crystallization experiment. As the T_g is frequency dependent, one can rationalize this seeming discrepancy by noting that the T_g determined with a time scale of a month would yield a value lower than the crystallization temperature. For almost all crystallizable polymers $T_m \gg T_g$; however, the blends illustrated here yield $T_m - T_g$ values as low as 15 °C. Longer annealing times or higher annealing temperatures could decrease this even to a negative value. This is, of course, a consequence of the frequency dependence of the T_g.

Phenoxy is only partially miscible with a commercial epichlorohydrin/ethylene oxide copolymer. While the phenoxy-rich phase T_g is significantly depressed, a residual phase consisting predominantly of the above-mentioned copolymer is observed based on T_g data. This result implies the possibility of compositional variation for the epichlorohydrin/ethylene oxide copolymer.

Phenoxy/poly(vinyl methyl ether) blends are opaque at processing temperatures or slightly above (e.g., 200 °C). When the blends are cooled, transparency is rapidly observed and reheating to the original temperatures leads to opacity. This reversible situation is characteristic of LCST (lower critical solution temperature) behavior as is commonly observed (as compared to upper critical solution temperature behavior) in polymer blends. This result offers thermodynamic justification of the miscibility of this blend.

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Excimer Formation in Dilute Solution. 1. Effect of Pressure on 1,3-Bis(2-naphthyl)propane and Poly(2-vinylnaphthalene)

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ABSTRACT: Excimer fluorescence is used as a probe of the bulk viscosity dependence of intramolecular segmental motion in dilute solution. The compounds studied are poly(2-vinylnaphthalene) (P2VN) of number-average molecular weight 300 000 and the dimer model compound 1,3-bis(2-naphthyl)propane ($\beta\beta$DNP). The viscosity of the toluene solvent is varied from 0.5 to 4.5 cP through application of hydrostatic pressures up to 450 MPa. The fluorescence behavior is analyzed in terms of Birks' scheme I kinetics for the photophysics and Kramers' theory for the segmental motion. The $\beta\beta$DNP data are fit satisfactorily by the Kramers treatment in the intermediate friction regime. The P2VN results, on the other hand, are fit better by the high-friction limit of the Kramers treatment, assuming that the effective local viscosity is different from the bulk solvent viscosity.

Introduction

The objective of this work is to examine intramolecular conformational rearrangement in dilute solutions of the aromatic vinyl polymers using excimer fluorescence as a molecular probe. Excimer formation in aromatic molecules is an important photophysical process which has been implicated in concentration quenching in solvents, in competitive excitation trapping in scintillator hosts, and as an intermediate step in photodegradation. Initial research efforts in the area were directed toward understanding the thermodynamics and kinetics of intermolecular excimer formation.[1,2] More recently, work has concentrated on the intramolecular process observed in model compounds and the aromatic vinyl polymers.[3]

Analysis of the photophysics of excimer formation in solution is complicated because sampling of suitable excimer-forming polymer chain conformations may result both from exciton migration and from rotational transformation due to solvent collision. Since only the second process is active in compounds containing two aromatic chromophores bound by a propane linkage, it may be possible to use information on these dimers to interpret excimer fluorescence in polymers. In this paper, 1,3-bis-(2-naphthyl)propane ($\beta\beta$DNP) is examined as such a model along with the corresponding polymer poly(2-vinylnaphthalene) (P2VN).

In most studies on the influence of bulk solvent viscosity on intramolecular excimer fluorescence, homologous solvent series[4] or solvent mixtures[5-8] have been used to achieve the viscosity variation. A possible difficulty in these approaches is that there may be large local variations in the solvent shell interactions with the isolated or complexed aromatic chromophores. Steric or specific chemical interactions between the solvent molecules and aromatic rings should affect both the rotational transformation process and the stability of the excimer complex once it is formed. This will be most significant when the solvents are chemically unrelated, as shown by Johnson.[4] To minimize this problem, hydrostatic pressure is used in this work to achieve a continuous variation in viscosity without changing the chemical character of the solvent shell. This variation can be appreciable; application of pressures to 450 MPa will cause the viscosity of toluene to increase from 0.5 to 4.5 cP.

The effect of pressure on intermolecular excimer formation has been the subject of several investigations.[9-17] These include studies on 1,2-benzanthracene, pyrene, perylene, and a number of naphthalene derivatives. The only pressure studies reported for intramolecular interactions have been on 1,3-bis(*N*-carbazoyl)propane.[13,14]

Experimental Section

A. Sample Preparation. 2-Ethylnaphthalene was obtained from Aldrich and used without further purification as a model compound for an isolated alkyl-substituted naphthalene ring, or monomer. 1,3-Bis(2-naphthyl)propane, the dimer model compound, was synthesized by a slight modification of the published

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