Macromolecules **1990,** *23,* 1225-1227

Communications to the Editor

Mathematical Modeling of the Effects of Annealing on Enthalpy Relaxations of Polymer Interfaces

In a recent publication[1,2] Quan et al. investigated relaxation phenomena in block copolymer systems. The specific system studied consisted of a styrene–hydrogenated butadiene–styrene triblock copolymer. Endotherms were observed in DSC experiments of samples annealed at temperatures well below the upper glass transition temperature of the styrene domains. The effect was explained by the enthalpy relaxation of material in the interfacial regions. They modeled the interface as a sequence of discrete fractions with T_g values between those of the blocks contributing independently to the excess enthalpy. Together with an additional assumption concerning the fully relaxed portion of the interface, the total amount of interfacial material could be evaluated.

Here a simple model will be formulated, which reproduces the experimental results of Quan et al.[1,2] and clearly illustrates certain complications associated with a correct estimation of the amount of interfacial material.

Following Quan et al., we assume that the interface consists of discrete fractions, which contribute independently to the relaxation process. For simplicity it is also assumed that T_g varies linearly through the interface from the lower T_g to the upper T_g, which in our case have been set equal to 273 and 373 K, respectively. The glass-forming kinetics of each fraction is described by the well-known four-parameter model introduced by Moynihan and co-workers.[3] Annealing will be treated as introduced into this approach by Hodge and Berens.[4,5] Cooling and heating are treated as a discrete set of temperature jumps, each jump followed by an isothermal hold of a time span corresponding to the cooling and heating rate. In the examples considered the cooling rate is 1000 K/min, whereas the heating rate is 20 or 30 K/min. Annealing takes place at an annealing temperature T_a = 300 K during the cooling cycle.

The calculation proceeds along the following lines. During the isothermal holds, the enthalpy relaxation toward equilibrium is described by the nonexponential decay function, $\phi(t)$

$$\phi(t) = \exp[-(t/\tau)^{\beta}] \qquad (1)$$

where β is the nonexponentiality parameter and τ a relaxation time. The relaxation of the enthalpy is expressed in terms of the fictive temperature T_f, which is defined as the temperature at which the enthalpy value observed would be the equilibrium value. The value of T_f after n steps is given by

$$T_f(n) = T_0 + \sum_{j=1}^{n} \Delta T(j)\{1 - \exp[-(\sum_{k=j}^{n} \Delta T(k)/Q(k)\tau(k))^{\beta}]\} \qquad (2)$$

Here T_0 is the starting temperature above T_g (in the examples considered T_0 = 400 K), $Q(k)$ is the cooling or heating rate, $\Delta T(j)$ is the temperature jump at the jth step, and $\tau(k)$ is given by

$$\tau(k) = A \exp[x\Delta h/RT(k) + (1-x)\Delta h/RT_f(k-1)] \qquad (3)$$

where x is the nonlinearity parameter, A a preexponential factor, R the universal gas constant, and Δh an activation enthalpy. During the annealing $\Delta T(k)/Q(k)$ is replaced by a set of annealing times, logarithmically even spaced in the interval (0, t_a), where t_a is the total annealing time (cf. ref 5). The normalized specific heat $C_p^N(T)$ is related to the fictive temperature by

$$C_p^N(T) = dT_f(T)/dT = [T_f(n) - T_f(n-1)]/[T(n) - T(n-1)] \qquad (4)$$

To model the interface, it is assumed to consist of a sequence of equal fractions of material with T_g's 2 deg apart. This is accomplished by choosing appropriate values for A, β, x, and Δh. The choice made is based on the following relation, which holds at temperatures $T \geq T_g$

$$\ln A = -\Delta h/RT + \ln \tau(T) \qquad (5)$$

Since $\tau(T_g)$ is approximately constant, independent of the value of T_g, T_g can be varied by varying ln A and/or Δh. For real systems the best fit values of A and Δh differ widely from system to system. Furthermore, the actual values turn out to be unrealistically small and large, respectively. It is impossible to attach physical significance to these numbers. However, at least for Δh a correlation between its value and the number of chain segments per relaxation event has been proposed.[6] In the modeling it is therefore assumed that A, β, and x remain constant for all fractions making up the interface, whereas Δh varies from fraction to fraction in agreement with the difference of 2 K between the consecutive fractions. Two different sets of parameters are choosen. Except for Δh, set 1 corresponds to polystyrene[7] (ln A = −216.4, β = 0.68, x = 0.43) and set 2 to poly(vinyl chloride)[5] (ln A = −274.0, β = 0.25, x = 0.35). These choices are motivated by the observation that annealing of PS and PVC, respectively, leads to enthalpy recovery peaks coincident with, or well below, their respective transition temperatures and therefore provides examples of diverse behavior.

Figure 1 shows the simulated DSC scans for sets 1 and 2 for various annealing times, together with the base lines obtained for a quenched run without annealing. Figure 2 shows the corresponding difference between the annealed and quenched runs. Finally, in Figure 3 the position of the maximum of the curves presented in the former figure is plotted against the logarithm of the aging times, t_a. Also additional results for a higher heating rate of 30 instead of 20 K/min are presented. The following features are observed:

(1) T_{max} increases linearly as a function of ln t_a. This comes as no surprise, since for pure components T_{max} also increases linearly with ln t_a and for a given annealing time the highest value for C_p^N is observed for $T_a \cong T_g - 20$. Hence, the maxima observed in Figure 2 correspond to those fractions of the interface that have a T_g of approximately 320 K (T_a = 300 K for the examples shown).

(2) As expected, the maxima corresponding to set 1 (e.g., PS) occur at a much higher temperature than those for set 2 (e.g., PVC). Furthermore, for reasonable values of t_a the respective peak maxima are located above and below the temperature of 320 K. This is consistent

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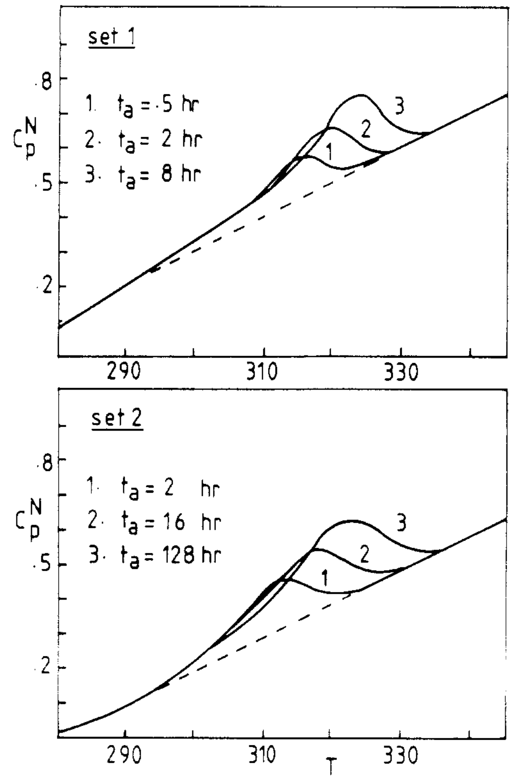

Figure 1. Calculated effect of annealing time on the development of heat capacity peaks of interfaces modeled using the parameters of set 1 and set 2 (see text). Dashed lines represent DSC traces of quenched samples: heating rate, Q = 20 K/min; annealing temperature, T_a = 300 K.

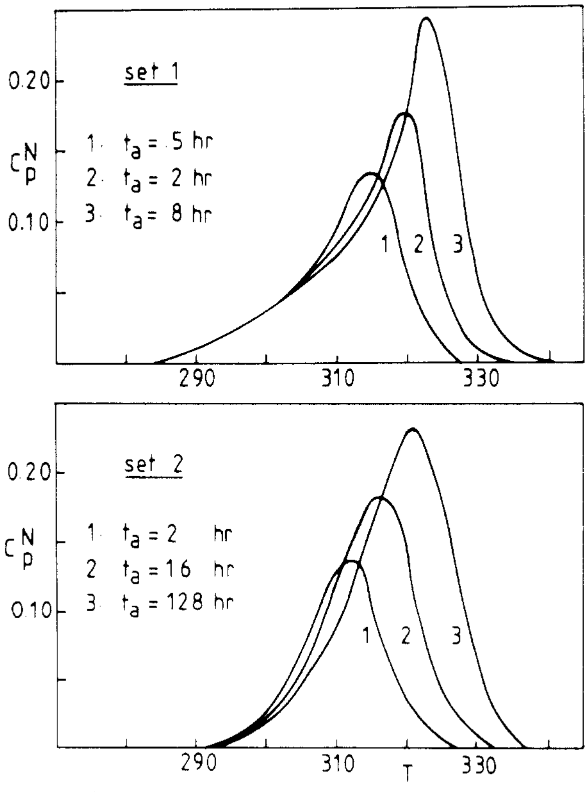

Figure 2. Calculated difference between DSC traces of annealed and quenched samples corresponding to the data of Figure 1.

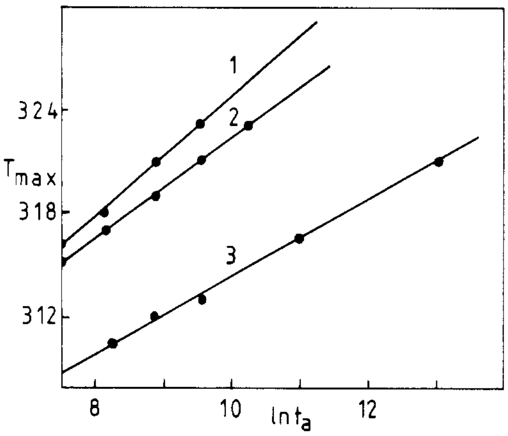

Figure 3. Calculated variation of T_{max} versus ln t_a (t_a, s). Curve 1: set 1, Q = 30 K/min. Curve 2: set 1, Q = 20 K/min. Curve 3: set 2, Q = 20 K/min.

with earlier comments concerning the enthalpy recovery peaks of pure PS and PVC, respectively, which appear above and below their respective glass transition temperature. This property is preserved if the Δh values are varied, which is the approach taken in the present simulation.

(3) Higher heating rates lead to higher T_{max} values. For a heating rate of 30 K/min and aging times of the order of 27 h the T_{max} belonging to set 1 (e.g., PS) is approximately 30 deg above the annealing temperature. This is in very good agreement with the observations of Quan et al.[1,2] on styrene–isoprene block copolymer systems.

Quan et al. used their data to estimate the amount of interface material. For this purpose they made the simplifying assumption that the fraction of the interface material with $T_g \leq T_{max}$ was fully relaxed. They observed that within experimental errors two enthalpy recovery peaks corresponding to two different aging times coincided up to T_{max} of the lowest peak (i.e., the peak belonging to the sample with the shortest aging time). Our calculations (Figure 2) indicate that, as a function of aging time, the endotherms shift slightly with respect to each other also at the low-temperature side. However, more serious complications arise, because enthalpy recovery peaks can occur well below as well as far above the glass transition temperature of the material involved. This has serious consequences for the position of the enthalpy recovery peaks of interfaces as demonstrated by Figure 3. Hence, the relation between the position T_{max} of the enthalpy peak and the T_g's of the fully relaxed portion of the interface depends strongly on the system at hand.

A final remark concerns the value of the relaxation enthalpy. In ref 1 experimental data for the relaxation enthalpy ΔH_{total} corresponding to that part of the relaxation endotherm for which $T \leq T_{max}$ values were presented. The same quantity can be estimated from the endotherms shown in Figure 2. To convert the normalized specific heat data, C_p^N into real specific heat data (i.e., J/g·K), an assumption concerning ΔC_p, the difference between the specific heat of the liquid and glass state, of each fraction has to be made. For simplicity a constant value of ΔC_p = 0.3 J/g·K, a characteristic value for many polymer systems, for all fractions of the interface dominating the relaxation process is taken. Furthermore, as in the case reported by Quan et al., it is assumed that 15% of all material involved is contained in the interface. On the basis of these assumptions, a value of $\Delta H_{total} \simeq$ 0.2 J/g is found for set 1 and t_a = 8 h. The same value is reported in ref 1 for a somewhat longer aging time of 25 h.

Considering all assumptions involved, the agreement between the numerical and experimental results is excel-

Macromolecules 1990, 23, 1227-1228

lent. It strongly supports the idea that an interface can be modeled as discrete fractions with T_g values between those of the pure components, contributing independently to the excess enthalpy.

Acknowledgment. The author gratefully acknowledges Dr. X. Quan for making ref 2 available prior to publication.

References and Notes

(1) Quan, X.; Bair, H. E.; Johnson, G. E. *Proceedings of the SPE 45th Annual Technical Conference & Exhibit*; 1987, p 1354.
(2) Quan, X.; Bair, H. E.; Johnson, G. E. *Macromolecules* **1989**, *22*, 4631.
(3) Moynihan, C. T.; et al. *Ann. N.Y. Acad. Sci.* **1976**, *279*, 15.
(4) Hodge, I. M.; Berens, A. R. *Macromolecules* **1981**, *14*, 1598.
(5) Hodge, I. M.; Berens, A. R. *Macromolecules* **1982**, *15*, 762.
(6) Hodge, I. M. In *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).
(7) Hodge, I. M.; Huvard, G. S. *Macromolecules* **1983**, *16*, 371.

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Received November 1, 1989
Revised Manuscript Received December 26, 1989

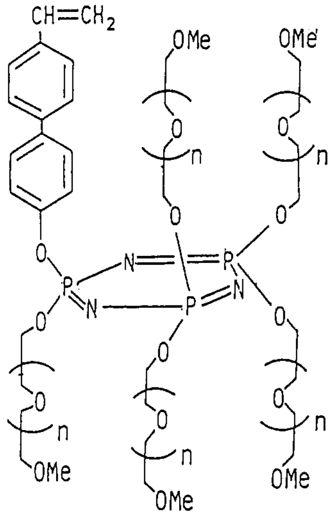
Polymerization of Vinyl Monomers Containing Oligo(oxyethylene)cyclotriphosphazene Derivatives and Binding of a Fluorescent Probe by Their Polymers

In previous papers,[1,2] we described the polymerization of vinyl monomers with pendant phosphazene groups such as 2-[(4′-vinyl-4-biphenylyl)oxy]pentachlorocyclotriphosphazene (1). Monomer 1 or its polymers can be modified by introducing functional groups by employing well-known phosphazene chemistry.[3] Cyclotriphosphazenes or phosphazene polymers with oligo(oxyethylenes) have been reported to be useful catalysts as phase-transfer reagents[4,5] or as ion-conducting solids.[6] These polymers have been prepared by the ring-opening/substitution method. We now report the polymerization of new multiarmed monomers, 2 and 3, which have five oligo(oxyethylene) chains on the phosphazene ring. The polymers would be expected to exhibit unique properties due to the large number of donor atoms. We also demonstrate preliminary results of the binding of a fluorescent probe by poly(2) and poly(3) (Chart I).

A typical procedure for the preparation of 2 is as follows. A solution of 1[1] (5.1 g, 10 mmol) in THF was added slowly to a solution of sodium 2-(2-methoxyethoxy)ethoxide, prepared from 2-(2-methoxyethoxy)ethanol (12 g, 0.1 mol) and NaH (2.4 g, 0.1 mol) in THF. The mixture was stirred for 10 h at room temppratature. After the usual workup, the reaction mixture was separated by column chromatography (silica gel, 1:9 methanol–chloroform) to give 4.0 g (43%) of 2. Monomer 3 was prepared by a similar procedure (yield 37%).

The radical polymerization of 2 or 3 with AIBN in various solvents at 70 °C gave polymers as shown in Table I. The polymers are highly viscous and soluble in common organic solvents and water. The IR data showed the presence of $-N{=}POCH_2-$ at 1220 cm^{-1}, and the elemental analysis supports poly(2) and poly(3). Separation of poly(2) and poly(3) from the monomers by a reprecipitation method is rather difficult. Therefore, the conversion was determined by the disappearance of vinylic protons using benzaldehyde as an internal standard.[7] The conversion was little affected by the length of oxyethylene chain. However, the conversion was strongly influenced by the solvent and correlated with the Taft and Kamlet β-value, for hydrogen bond acceptor basicities.[8] This indicates that hydrogen-bond formation is the most important factor in polymerization of 2 and 3. Number-average molecular weights (M_n) of the polymers obtained in ethanol and 2-propanol are higher than those in benzene and 1,2-dichloroethane (DCE). The results are opposite to those predicted from chain-transfer constants of the solvents. Hydrogen-bond interaction would lead to a change in both the polymerizability of the monomers and the propagation rate due to a change in concentration of monomer around the propagating polymer radical.[9] In DCE, the propagating polymer radical would interact more strongly with the monomer than with the solvent. This implies that increasing monomer concentration around the growing polymer radical increases the propagating rate. However, this was not the case. In order to clarify the solvent effect on monomer reactivity, ^{13}C NMR spectra were measured. The β-carbon peak of the vinyl group of 2 in DCE and in ethanol appeared at 113.5 and 114.8 ppm (from TMS), respectively. For 1, neither the chemical shift nor the conversion was affected by solvents. From these results, the change in reactivity due to interaction between monomer and solvent is likely to be one of the important factors for the acceleration of polymerization in ethanol. Furthermore, the fact that the intrinsic viscosity of poly(3) (M_n = 50 000) in ethanol ($[\eta]_0$ = 0.10 at 30 °C) is lower than that in ben-

Chart I



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2 ;	1
3 ;	2

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