Registry No. (MMA)(MS) (copolymer), 28429-02-9; (MMA)(HEA) (copolymer), 27756-39-4; PHMP, 9003-35-4; *p*-F-PHMP, 26045-02-3; *p*-Cl-PHMP, 26045-03-4; *p*-Br-PHMP, 26045-04-5; *p*-NO_2-PHMP, 27322-28-7; *p*-OCH_3-PHMP, 38639-99-5; *p*-CH_3-PHMP, 25053-88-7; Varcum 2217, 121674-18-8; KOH, 1310-58-3; NaOH, 1310-73-2; RbOH, 1310-82-3; CsOH, 21351-79-1; $(CH_3)_4NOH$, 75-59-2; $(C_2H_5)_4NOH$, 77-98-5.

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On the Physical Meaning of the Kwei Equation for the Glass Transition Temperature of Polymer Blends

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ABSTRACT: Poly(vinyl cinnamates) substituted with electron-donor or -acceptor groups in the para position of the phenyl ring and similar vinyl polymers where the substituted cinnamoyl groups are separated from the main chain by $(CH_2)_3$ and $(CH_2)_6$ spacers were prepared. The glass transition temperatures of 12 miscible pairs of these polymers were determined as a function of composition, and the T_g versus composition curves were approximated by an empirical equation proposed earlier by Kwei:[2] $T_g = (w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2) + qw_1w_2$. By classifying the systems according to the values of the constants k and q, certain regularities of behavior became apparent, which led to a physical interpretation of this equation. It is suggested that, in the important class of systems where $k = 1$, the constant q represents the stabilization energy of the backbone in the blend in excess of the weighted mean of the stabilization energies of these components. This interpretation is supported by the results of photoreactivity measurements. Systems where $k \neq 1$ and $q \neq 0$ have S-shaped T_g versus w curves. These are characteristic of incipient phase separation.

In a study of the photosensitivity of substituted poly(vinyl cinnamates), a series of blends of electron-donor- with electron-acceptor-substituted polymers was prepared.[1] To test the compatibility of the polymers with each other and detect the possible appearance of a second phase, the glass transition of the blends was monitored as a function of composition. The experimental data were fitted by an equation proposed in 1984 by Kwei.[2] Certain regularities observed in the T_g versus composition curves invited further investigation, which led finally to a qualitative interpretation of the characteristic constants of the Kwei equation.

The thermodynamic criterion for compatibility is a negative value of the free energy of mixing of the components:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

Since the entropy of mixing of high polymers is always small, the coexistence of two polymers in the same phase is predicated by a negative enthalpy of mixing, $\Delta H_m < 0$, corresponding to an attractive interaction between the components. This has been understood for a long time[3] and miscible polymer blends have been formulated on the basis of various secondary interaction forces, such as hydrogen bonding,[2,4] ion–dipole forces,[5] and electron-donor–acceptor interactions.[6,7] In this study we had available a series of polymer blends in which the strength of electron-donor–acceptor interactions in the side chains had been systematically varied, while keeping the basic structure of the backbone constant. It was found in preliminary experiments that the glass transition was affected by these interactions, we have therefore undertaken a systematic mapping of the T_g of the blends of these polymers. To estimate the nature and the degree of side-chain interaction, we have also determined the photoreactivity of the blends and have tried to understand the relation between the two phenomena.

Because of the link of the glass transition with the mechanical and thermal properties of polymer blends, the dependence of the glass transition temperature on composition has received much attention. Several equations are available to describe this relationship in empirical

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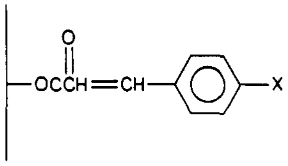
terms. We mention the Gordon–Taylor equation,[8] the Jenkel–Heusch equation,[9] and the equations proposed by Fox,[10] by Couchman,[11] and by Kwei.[2] Of these, only the Kwei equation

$$T_g(1,2) = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + q w_1 w_2 \qquad (2)$$

is able to represent all our data adequately. (The rather complex equation recently proposed by Breckner et al.[12] was also able to fit the data.) We have used the constants k and q in eq 2 as a classification principle for our results. In so doing we became aware of some qualitative correlations between the thermal behavior of blends and, principally, the values of q. A combination of this with the photochemical behavior of the systems and a closer look at the events that occur at the glass transition of a blend of two polymers has led us to propose a qualitative physical interpretation for the constants of eq 2.

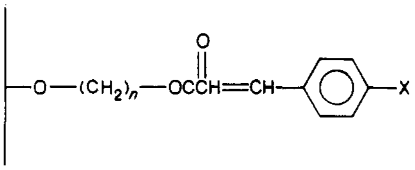
Experimental Section

Two kinds of polymers were used in this study: (a) Poly(vinyl cinnamates) substituted in the para position of the phenyl ring. These have the generic structure



Here X is either an electron-donating substituent, such as OCH_3 and CH_3, or an electron-withdrawing substituent, such as Cl, $OOCCH_3$, and CN.

(b) Polymers based on the same reactive moieties as above, but with spacer groups separating the backbone from the cinnamoyl groups in the side chain



n = 3 or 6

The individual polymers and their blends are referred to in the text by the self-explanatory acronyms P-OCH_3, P-Cl, P-3-OCH_3, P-6-OCH_3, P-Cl/P-OCH_3, and so on.

Substituted poly(vinyl cinnamates) were prepared by the functionalization of a single batch of poly(vinyl alcohol) obtained from Eastman Kodak (MW 300 000) (see ref 1). The synthesis of the polymers containing the methylene group spacers is described in a forthcoming paper.[13]

The glass transition temperature was determined from thermograms obtained with a Du Pont Model 910 differential scanning calorimeter. The experiments were run under nitrogen at a heating rate of 15 deg/min. The heating rate and the thermal treatment that the sample received had some effect on the thermograms, a heating rate of 15 deg/min seemed optimum. Annealing made the secondary phase transition more pronounced, indeed in some samples it was hard to determined the glass transition without careful annealing. A standard procedure was finally adopted that allowed a uniform treatment of all samples and produced clearly readable glass transitions: The samples were first vacuum-dried at room temperature, and prior to the calorimetric experiment were prebaked for 30 min in a vacuum oven at a few degrees below the expected T_g. The value of T_g was read at the midpoint of the transition.

As a measure of the photochemical sensitivity of the blends, which is related to the donor–acceptor properties of the substituents,[1] we determined the gel point exposure dose, E_G. This is the minimum exposure leading to insolubilization of the cross-linked polymer. To measure E_G, polymer films were coated on quartz plates and were exposed, after drying, to monochromatic radiation from a Bausch and Lomb monochromator–lamp combination. After exposure the films were washed in solvent and the exposure dose for incipient insolubilization (gel formation) was determined. For details of the procedure, see ref 14.

The distribution of site reactivities in solid films of the blends was derived from the dependence on reactant conversion (x) of the overall quantum yield ϕ of the photoreaction. This was measured by monitoring the change in the absorption spectrum of the reactant on irradiation. The quantum yield function $\phi(x)$ is linked to the distribution function $f(q)$ of site reactivities q by a set of equations[18] that allow calculation of $\phi(x)$ for any given reactivity distribution. By starting with a reasonable trial distribution and modifying it until the corresponding $\phi(x)$ curve fits the experiment, the actual distribution of site reactivities can be established. The distribution of site reactivities is usually presented in the form of a histogram with the frequency of occurrence of a reactivity value q plotted against q. A description of the method of site reactivity analysis can be found in ref 17 and 18.

Results

Of the 66 possible combinations of the 12 polymers prepared in this study, only 12 pairs formed miscible blends. The glass transition temperature of these blends was measured as described above and plotted as a function of composition. The T_g versus w curves of the miscible blends are shown in Figure 1. The full lines represent the Kwei equation, which produces the best fit of the experimental data.

The diagrams are presented in four groups corresponding to different sets of values of the parameters k and q.

Discussion

Algebraic Analysis of the Kwei Equation. Equation 2 can be rewritten in terms of the weight fraction w of component 2.

$$T_g = \frac{T_{g1} + w(kT_{g2} - T_{g1})}{1 + w(k - 1)} + q(w - w^2) \qquad (3)$$

For the important case of a system where $k = 1$, derivation of (3) with respect to w shows that the function has an extremum at the point

$$w = \frac{T_{g2} - T_{g1} + q}{2q} \qquad (4)$$

the second derivative of (3) being

$$(\mathrm{d}^2 T_g/\mathrm{d}w^2)_{k=1} = -2q \qquad (5)$$

This means that if $k = 1$, the T_g versus w curve will have no inflection point and that the extremum will be a maximum for $q > 0$ and a minimum for $q < 0$. Furthermore, at $w = 0.5$ the tangent to the T_g versus w curve will be parallel to the straight line joining $T_{g1}(w{=}0)$ and $T_{g2}(w{=}1)$.

$$(\mathrm{d}T_g/\mathrm{d}w)_{w=0.5} = T_{g2} - T_{g1} \qquad (6)$$

All these points are illustrated by the systems shown in Figure 1.

The Meaning of q. A simple interpretation of eq 2 can be given for the case $k = 1$. In that case, eq 2 can be written in the form

$$T_g = (w_1 T_1 + w_2 T_2) + q w_1 w_2 \qquad (7)$$

where the two terms in parentheses represent the weighted mean of the glass transition temperatures of the polymeric components and the term $q w_1 w_2$ represents the deviation of the glass transition temperature of the blend from that

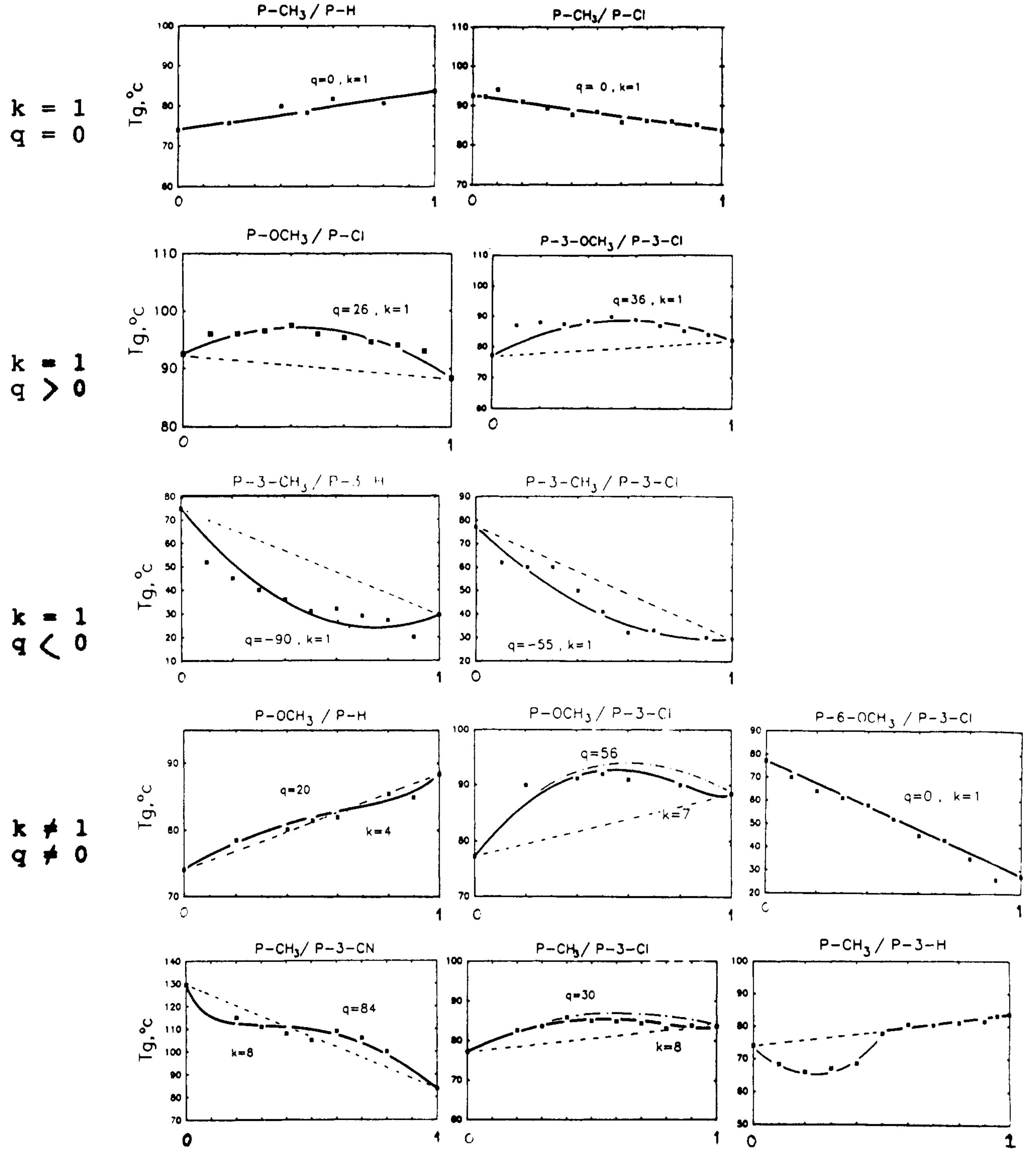


Figure 1. Glass transition temperature (°C) plotted as a function of composition (weight fraction of the electron-donor-substituted component). The identity of the polymer pairs is indicated in the diagrams.

weighted mean. It is generally accepted that the glass transition is associated with the incipient motion of the polymer backbone.[15] The product k_BT_g, where k_B is the Boltzmann constant, is therefore the average thermal energy just sufficient to overcome the energy barriers that, below T_g, immobilize the backbone. The term energy barrier includes here both intramolecular flex energy and intermolecular hole energy.[15] The product $k_Bqw_1w_2$ is then the excess energy by which the average stabilization of the backbones in the blend is greater than the weighted average in the backbone stabilizations in the homopolymers. If that excess energy is positive ($q > 0$), it will lead to a higher glass transition temperature in the blend. If the backbone stabilization in the blend is smaller than the weighted average of the backbone stabilization of the pure components ($q < 0$), the excess stabilization energy will be negative and the glass transition temperature of the blend will be lower than the mean glass transition temperature of the homopolymers.

The sources of backbone stabilization are ultimately the contacts that are formed in the solid matrix between elements of the main chain and its environment. It is not possible to treat this situation with any accuracy because even the concept of backbone is not exact, and in the concept of "environment" all structural elements that contribute to the immobilization of the backbone should be included. However, the situation can be visualized crudely in terms of a lattice model (see Figure 2) where

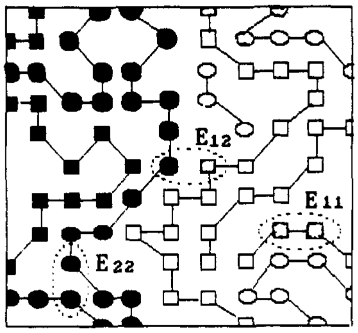


Figure 2. Lattice model of a blend of two polymers (1,2). Three typical contact pairs and their contributions E_{ij} to backbone stabilization are indicated.

every chain element of the backbone occupies a single site. In the blend there will be homocontacts between two units of polymer 1, homocontacts between units of polymer 2, and heterocontacts between a unit of polymer 1 and a unit of polymer 2. If the volume fractions of such contacts in the system are indicated by ϕ_{11}, ϕ_{22}, and ϕ_{12}, and their contributions to backbone stabilization by E_{11}, E_{22}, and E_{12}, the excess backbone stabilization energy in the blend over the weighted mean stabilization in the homopolymers can be expressed in the form

$$k_Bqw_1w_2 = \phi_{12}E_{12} + \phi_{11}E_{11} + \phi_{22}E_{22} - 0.5(E_{11} + E_{22}) \tag{8}$$

Equation 8 has the form of the energy of mixing in solution, the difference is that here it refers to a solid system and exclusively to the state of the backbone.

In terms of the lattice model of Figure 2, ϕ_{12} is the probability of finding a mixed pair of units 1 and 2 at any location in the lattice. This probability will of course depend on the composition of the system. To estimate it we shall consider only nearest neighbors and assume a coordination number of 6 for each site. This means that each backbone unit will be surrounded by six other such units. Two of these will be members of the same chain and will therefore be of the same kind; the remaining four positions will be statistically distributed between homocontacts and heterocontacts, in proportion to the volume fractions (or weight fractions) of the two components. Thus the probability that any unit of component 1 will form a heterocontact pair is $(4/6)w_2$ and the probability of finding such a heterocontact pair anywhere in the system is $(4/6)w_1w_2$.

These primitive statistics apply of course only if the units are distributed at random. In a blend of polymers this will not be the case, and considerably more complex statistics would have to be used for a more realistic description of the system. (See, e.g., the chapter on polymer melts in ref 16.) For the purpose of this discussion, it is, however, sufficient to say that the volume fraction of heterocontact pairs is proportional to the product $(2/3)w_1w_2$

$$\phi_{12} = f(2/3)w_1w_2 \tag{9}$$

where f may be termed a dispersion factor, because it will depend on the completeness of the intermixing of the two homopolymers as well as on the effect of the connectedness of neighboring chains.

By use of eq 9 and elimination of ϕ_{11} and ϕ_{22}, eq 8 may be written in the form

$$q = \frac{2f}{3k_B}[E_{12} - 0.5(E_{11} + E_{22})] \tag{10}$$

where k_B is the Boltzmann constant.

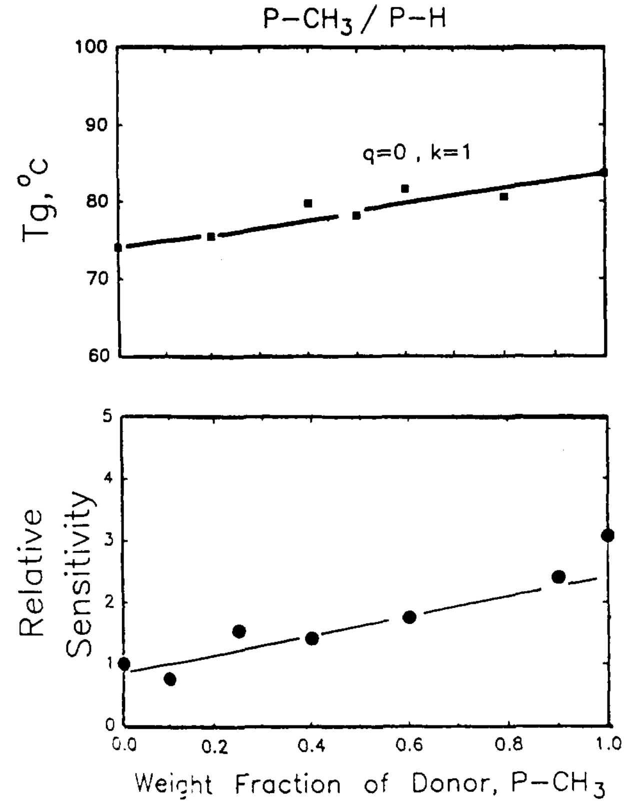


Figure 3. Curves of T_g and of photosensitivity versus composition for a pair with $k = 1$ and $q = 0$, namely, P-H/P-CH$_3$.

The case $k = 1$, $q = 0$ is considered first. In that case the bracket in eq 10 must be zero:

$$E_{12} = 0.5(E_{11} + E_{22}) \tag{11}$$

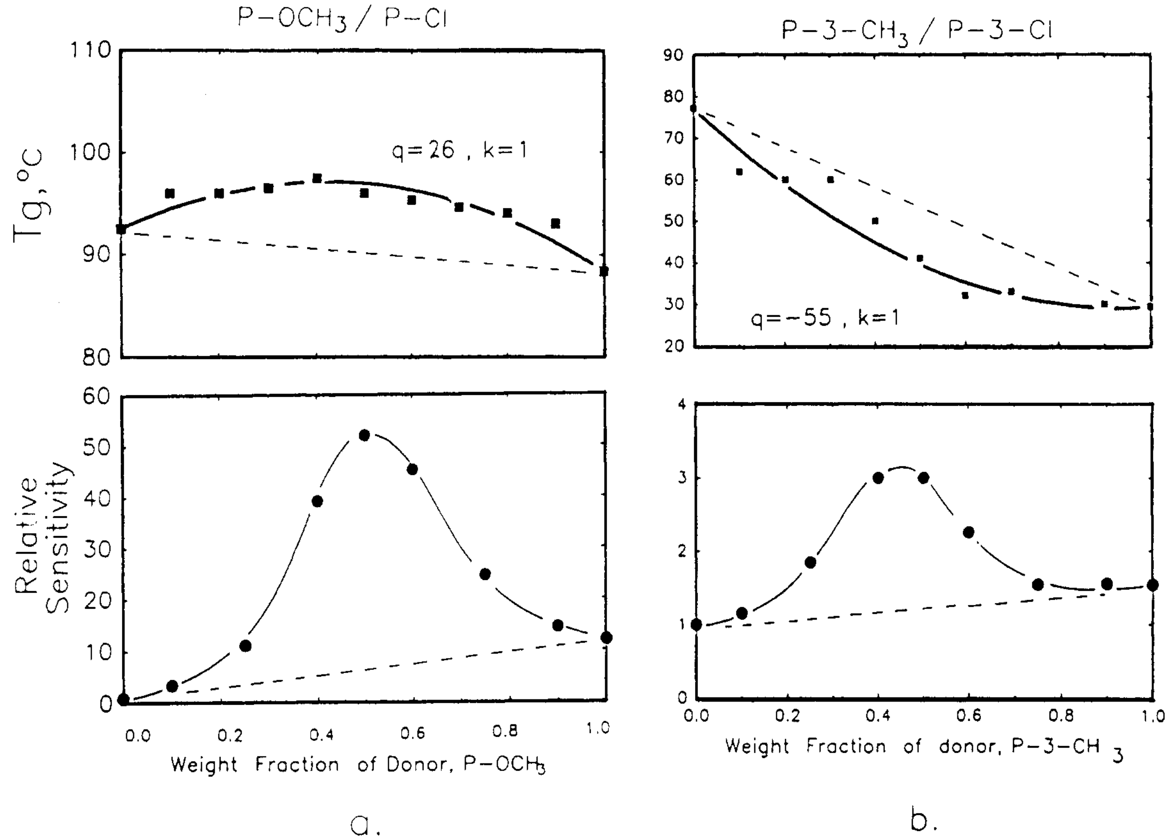
If the contact energies between units of the two homopolymers are (almost) the same, condition 11 shows that the energy of the heterocontacts will be almost identical with that of the homocontacts; i.e., the units of both polymers can substitute for each other with minimal disturbance to the solid system, so that formally

$$E_{12} = E_{11} = E_{22}$$

If, however, the homocontacts of the two components are very different, then condition 11 will be met when E_{12} is the arithmetic mean of the energies of the homocontacts. In that case the loss in stabilization on mixing suffered by the component with the higher T_g is (almost) exactly balanced by the gain in stabilization experienced by the other component.

The case of $k = 1$, $q = 0$ is illustrated in Figure 1 by two pairs of polymers: P-H/P-CH$_3$ and P-Cl/P-CH$_3$. Here interaction between the (photoreactive) side chains is weak, and the steric requirements of the components are not too different. In that case the contact energies of the heteropairs and the homopairs will be similar. This view is supported by the fact that the photosensitivity of the blends is also the weighted mean of the photosensitivities of the homopolymers (see Figure 3). The significance of the photoreactivity data in this context is that the increase in photoreactivity measures the number of heterocontacts above the random statistical average that have formed in the blend.

In the pair P-Cl/P-CH$_3$ the interaction between the side chains is stronger, but so is the stabilization energy of the Cl-substituted homopolymer, which has a higher T_g than P-CH$_3$. In this case the two polymers would be incom-



a. b.

Figure 4. Curves of T_g and of photosensitivity versus composition for (a) the pair P-Cl/P-OCH$_3$ where $k = 1$ and $q > 0$ and (b) the pair P-3-Cl/P-3-CH$_3$ where $k = 1$ and $q < 0$.

patible were it not for this side-chain interaction. Here the energy of the heterocontacts must be equal to the arithmetic mean $0.5(E_{11} + E_{22})$.

The case $k = 1$, $q > 0$, where $E_{12} > 0.5(E_{11} + E_{22})$, is illustrated in the pairs P-Cl/P-OCH$_3$ and P-3-Cl/P-3-OCH$_3$. Here interaction between the side chains is again strong (see the photosensitivity curve in Figure 4a), and the backbone is, therefore, stabilized well in excess of the mean stabilization energy of the homopolymers.

At this point it is of interest to have an estimate of the absolute magnitude of the excess stabilization energies in terms of the the overall stabilization of the backbone. The q values in the two pairs just mentioned are $q = 26$ and $q = 36$, respectively. Consider one mole of backbone monomer units of a 50:50 blend that has a q value of 50. The excess stabilization per mole will be

$$Rqw_1w_2 = 0.002 \times 50 \times 0.5 \times 0.5 = 0.025 \text{ kcal/mol}$$

where R is the gas constant (which has a value of about 0.002 kcal/grad). Compare this with the overall backbone stabilization of a polymer having a T_g of 100 °C.

$$RT_g = 0.002 \times 373 = 0.746 \text{ kcal/mol}$$

It can be seen that even with $q = 50$, which is a large value of the Kwei constant q, the fraction of the excess energy in the overall stabilization is quite small, slightly more than 3% (0.025:0.746 = 0.033). The glass transition temperature is a very sensitive monitor of changes in the stabilization energy of the backbone.

The case $k = 1$, $q < 0$ is now considered. At first it would seem that with a negative value of q the polymers should be imcompatible, but that is not necessarily so: While the enthalpy of mixing must be negative for the two polymers to be compatible, and the overall interaction between the polymers must therefore be attractive, if interaction in the vicinity of the backbone alone determines T_g, there may still be a reduction of the energy barrier to backbone movement. This is illustrated in Figure 1 by the

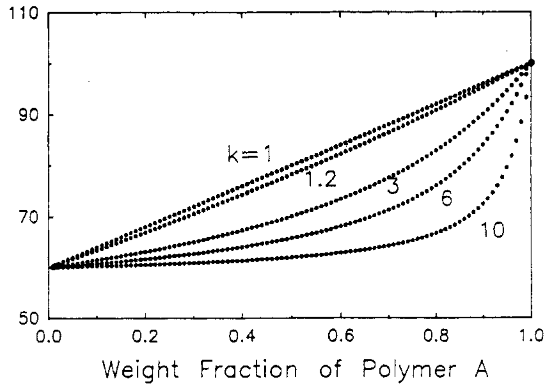


Figure 5. T_g calculated by the Gordon–Taylor equation (or the Kwei equation with $q = 0$) for a range of k values and plotted as a function of composition (weight fraction of one component).

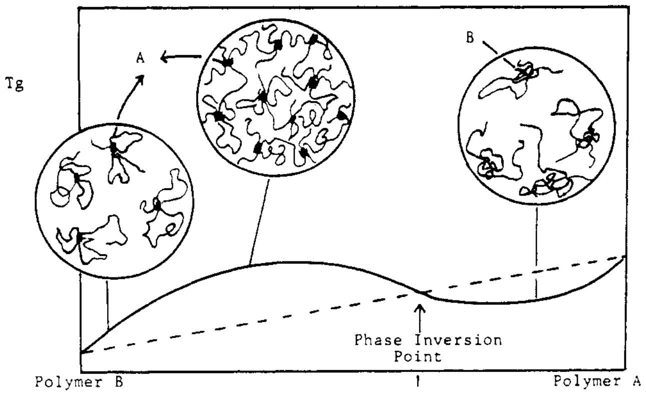


Figure 6. Schematic illustration of the microphase-separated system of a polymer pair with $k \neq 1$ and $q \neq 0$.

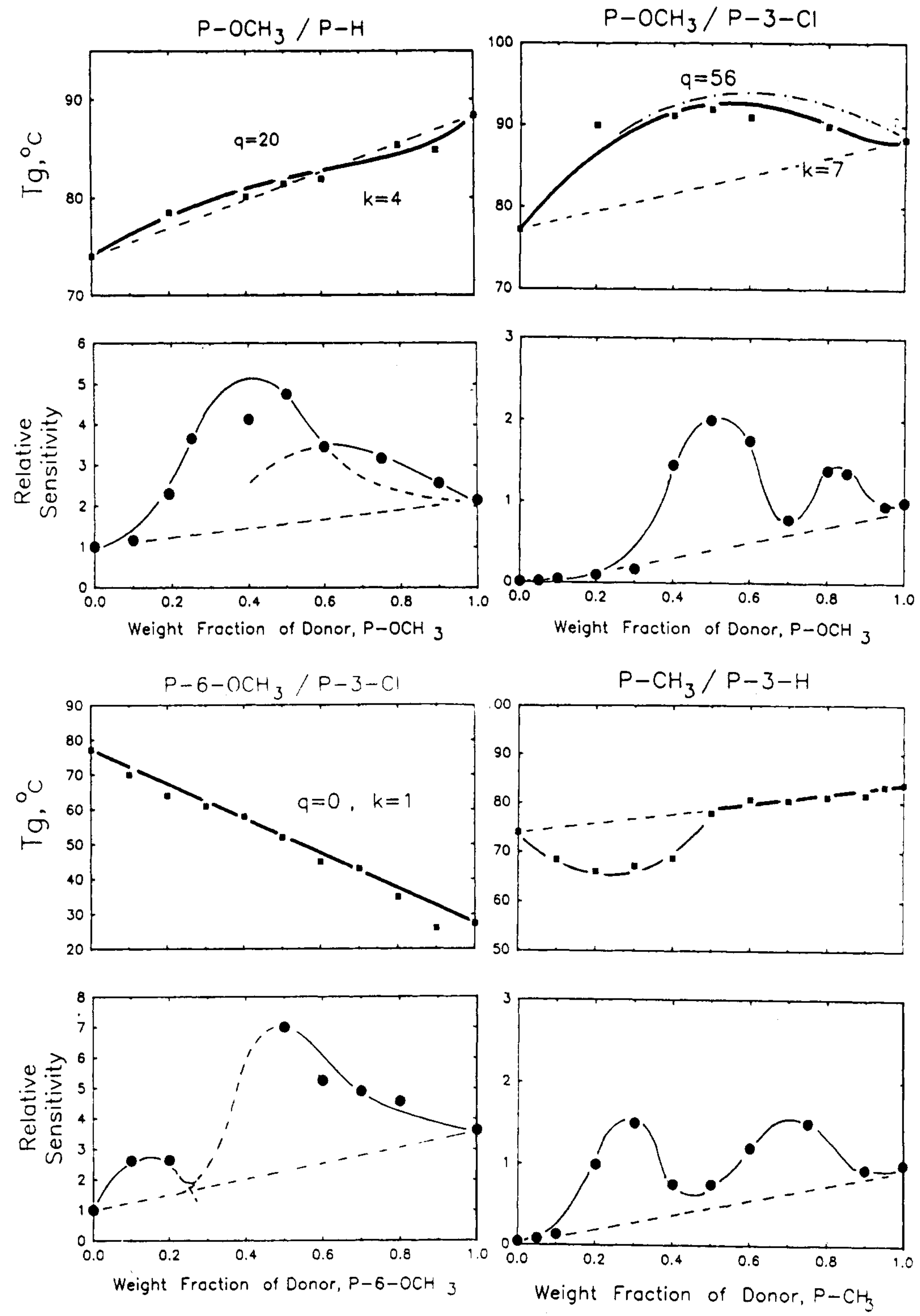


Figure 7. Curves of T_g and photosensitivity versus composition for four microphase-separated systems with $k \neq 1$ and $q \neq 0$. Note that in all these systems the photosensitivity curves have two maxima and that the T_g curves have an inflection point.

pairs P-3-H/P-3-CH_3 and P-3-Cl/P-3-CH_3. In both cases there is significant local alignement of the side chains, as evidenced by the photosensitivity curve of the blends in Figure 4b. This interaction would contribute to the miscibility of the two polymers. However, the glass transitions of the two homopolymers are far apart, indicating significant differences in the cohesive energies and the packing densities of the homopolymers. In bringing the two components together the main chains of the polymers may be less well packed in the blend, causing a lowering of the energy barriers at the backbone which the interaction of the decoupled side chains cannot fully compensate. As a result q is negative and the glass transition of the blends lies below the weighted mean of the glass transitions of the homopolymers. Here again, the (negative) excess energy in the blends amounts to not more than a few percent of the overall stabilization of the backbone.

The Meaning of *k*. It k is not equal to one ($k \neq 1$), but $q = 0$, the Kwei equation reduces to the Gordon–Taylor equation[8]

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \tag{12}$$

Several interpretations have been suggested for the constant k in the Gordon–Taylor equation. It is thought to represent the ratio of the volume expansion coefficients

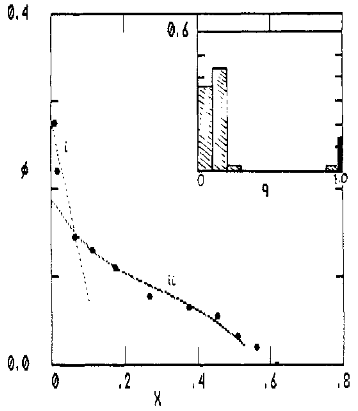


Figure 8. Quantum yield versus composition curve, $\phi(x)$, and histogram of the site reactivity distribution for a 50:50 blend of the pair P-3-Cl/P-OCH_3. Note the two branches of the $\phi(x)$ curve corresponding to two distinct population of pair sites (see text).

of the components at the glass transition temperature[8] or the ratio of the heat capacity increments[11] of the components. Either one or both of these interpretations may be valid in the range of k values (0.8–1.2) in which the Gordon–Taylor equation successfully describes the behavior of miscible blends.

That the Gordon–Taylor equation is limited in its applicability is in part caused by the fact that deviations of T_g from the weighted mean of the homopolymers are expressed exclusively by k and that at the same time the constant k, which is associated with the weight fraction of only one of the components, introduces asymmetry into the T_g versus w curve. Derivation of (12) shows that the Gordon–Taylor equation can have neither an extremum nor an inflection point, and this is illustrated in Figure 5, which refers to a hypothetical set of polymers that have the glass transition temperatures T_{g1} = 60 °C and T_{g2} = 100 °C and values of k ranging from 1 to 10.

In the Kwei equation the situation is different: when k is not unity ($k \neq 1$) and q is not zero ($q \neq 0$) the T_g versus w curves have extreme *and* an inflection point and must, therefore, always be S shaped. This has an interesting consequence; it means that the system changes from a state of increased to a state of decreased backbone stabilization. In the amorphous matrix the two states must correspond to different molecular morphologies.

The case $k \neq 1$, $q \neq 0$ is illustrated in Figure 1 by six pairs of polymers: P-H/P-OCH_3, P-3-Cl/P-OCH_3, P-3-Cl/P-6-OCH_3, P-3-CN/P-CH_3, P-3-Cl/P-CH_3, and P-3-H/P-CH_3. It will be noted that these systems are characterized by a large steric mismatch in their structures. With one exception, the pairs are made up of components that differ in the length of the spacers between backbone and the reactive part of the side chain. Such systems usually have a strong tendency to phase separation. We believe that microphase separation does occur in the systems of the present group and that consequently the electron-donor–acceptor interactions between the side chains can express themselves only accross the phase boundaries. These interactions tend to maximize the interphase surface and to minimize the volumes of the individual phases. As a result, the systems are in a state reminiscent of that encountered in some segmented block copolymers. Figure 6 is a schematic which shows how the roles of the dispersed phase and the continuum phase are switched at the point of phase inversion; it also shows that the point of inversion correlates with the inflection point of the T_g versus w curves.

This view of the polymer blends with S-shaped T_g curves is also supported by the results of photosensitivity measurements shown in Figure 7. The sensitivity curves have two maxima correlated with the two lobes of the T_g versus w curves, indicating that the two microphase-separated states differ in the arrangement of the photosensitive reactants. Also, the point of phase inversion is correlated qualitatively with a region of low photosensitivity, i.e., minimum reactant ordering in the amorphous matrix.

Indirect evidence for donor–acceptor interaction across the phase boundaries in blends with S-shaped T_g curves is further provided by the site reactivity distributions in these systems. The distribution of reactivities over reactant sites in the solid matrix is represented by a histogram where the frequency of occurrence of a reactivity value is plotted against the value (0 to 1) of that reactivity. The histogram in Figure 8 represents the distribution of site reactivities in the 50:50 blend of the pair P-3-Cl/P-OCH_3. It shows clearly two separate populations of reactive sites: a small group (13%) of highly reactive sites, which are associated with the heterocontact pairs across the phase boundary, and a large population (87%) of low reactivity sites, corresponding to the homocontact pairs within the bulk of the microphases.

A comment on the systems represented in the last section of Figure 1 and in Figure 7 is in order. In the systems P-3-Cl/P-6-OCH_3 and P-H/P-OCH_3 the deviations of the experimental values of T_g from the weighted average of the homopolymers are within the accuracy of the measurement, and the tracing of the T_g versus w curves given in the figures would not be a priori justified. However, in view of the results of the photoreactivity measurements and of the foregoing discussion, we believe that it is appropriate to include these two systems in the groups of S-shaped T_g curves. Further, the T_g curve of the pair P-3-H/P-CH_3 has a highly unusual shape. We have remeasured this system several times and are now convinced that the T_g curve of this system is correct as shown, although it is not possible to approximate it successfully by eq 2.

A final remark concerns the physical meaning of the constants k and q in the general case represented by the S-shaped T_g versus w curves in Figure 7. When the curves are highly asymmetric, such as in the case of the pairs P-3-Cl/P-OCH_3 and P-3-Cl/P-CH_3, values of k = 7 and k = 8 are required to fit the data. Such high values of k on their own (i.e., with q = 0) will produce large negative deviations from the weighted mean of the glass transition of the components (see the curves in Figure 5). To compensate for this in the convex lobes of the T_g curves, larger values of q are needed than would be expected in systems that are not asymmetric and where k = 1. It follows that in the asymmetric systems the value of q is no longer the sole measure of the excess stabilization of the backbone. In the general case k = 1, q = 0 the constants k and q are empirical fitting parameters and can no longer be identified separately with different physical properties of the system.

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Registry No. Poly(vinyl alcohol) *p*-methylcinnamate, 121288-48-0; poly(vinyl alcohol) cinnamate, 9050-06-0; poly(vinyl alcohol) *p*-chlorocinnamate, 121288-47-9; poly(vinyl alcohol) *p*-methoxycinnamate, 121288-46-8.

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Notes

Dynamics of Copolymer Solutions Determined by Using Neutron Spin-Echo

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I. Introduction

In this paper we present an experiment recently made on the spin-echo spectrometer IN11 of the Institut Laue Langevin (ILL, Grenoble) which we believe shows unambiguously for the first time the internal motion of a chain in solution.

It has been shown,[1] by using the random-phase approximation (RPA), that a solution of two homopolymers always exhibits two relaxation modes. This allows us to write for the intermediate scattering function $S(q,t)$

$$S(q,t) = A_c e^{-\Gamma_c t} + A_I e^{-\Gamma_I t} \tag{1}$$

where q is the scattering vector ($q = 4\pi/\lambda \sin \theta/2$), λ is the wavelength of the incident radiation in the medium, θ is the scattering angle, and t is time. Γ_c and Γ_I are the characteristic frequencies attributed to the so-called cooperative and interdiffusion modes. They depend on the nature of the two homopolymers, their concentration, and the thermodynamic interaction parameters. The amplitudes A_c and A_I depend on the contrast factors and other physical properties of the system.

These conclusions have been verified experimentally[2-4] by quasi elastic light scattering, and without going into details there is a good agreement between the theoretical predictions and the experimental results.

This theory has been extended to one copolymer (mainly two blocks of A–B type copolymer) in solution[5] leading to a formula identical with eq 1. The theoretical expression of the quantities (A_c, A_I, Γ_c, and Γ_I) and their variations with concentration, composition, and other physical parameters have been discussed elsewhere in detail.[5,6] They are different from those obtained for a mixture of two homopolymers in solution. In this case, the relaxation frequency Γ_c corresponds to the cooperative motion of the pseudonetwork formed by the two species in solution. Its value is identical with that which could be obtained for a homopolymer of the same length and the same thermodynamical properties. The relaxation frequency Γ_I has been identified as describing the relative motion of one block with respect to the other.

Our interest was focused on this latter mode, and the purpose of this experiment was to find experimental conditions for which the amplitude A_c of the cooperative mode vanishes, thus allowing one to observe only the interdiffusion mode. The calculation shows that for a 50/50 diblock copolymer if one adjusts the total contrast factor of the solvent in order to satisfy the relation

$$(a_H - a_o)x + (a_D - a_o)(1 - x) = 0 \tag{2}$$

or

$$a_H x + a_D(1 - x) = a_o \tag{3}$$

then $A_c = 0$. In these relations, a_H, a_D, and a_o are the coherent scattering length per unit volume of the ordinary polymer, the deuterated polymer, and the solvent, respectively, and x is the volume fraction of the nondeuterated block within the copolymer. This condition has been called the "optical θ point" by Tanaka and Inagaki[7] in the case of a light-scattering experiment. It corresponds to a "zero average contrast" of the copolymer. For a monodisperse system, this leads to a zero scattering intensity at zero angle ($q = 0$). Therefore, it is of particular interest to work under these experimental conditions for a precise determination of the interdiffusion mode.

II. Experimental Section

A. Sample Preparation. In order to avoid incompatibility effects and ensure good solubility, a diblock copolymer of deuterated styrene–ordinary styrene was prepared. Its characterization was carefully made by light scattering, GPC, NMR, and small-angle neutron scattering (SANS).[8] The details are given in a recent paper,[8] and the results are collected in Table I. The neutron-scattering experiments were made on a mixture of ordinary and deuterated benzene. In order to obtain zero average contrast, we used, as in ref 8, a mixture made of 51.3% ordinary and 48.7% deuterated benzene. Since the level of intensity depends on the polymer concentration, it is advantageous to work at high concentration. In fact, we used only one concentration, $c = 0.34$ g/cm^3, since the theory,[5] which has been verified experimentally,[8] predicts that the shape of the intensity of the signal is concentration independent. Since the polymer is of a relatively low molecular weight, the solution is not too viscous at this concentration and can be handled easily. Moreover, this concentration corresponds to the so-called semidilute regime (c is of the order of $3c^*$, where c^* is the overlap concentration) where the theory is more appropriate.

B. Neutron-Scattering Experiments. Neutron-scattering experiments were performed at the ILL, Grenoble, using the NSE

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