Viscoelastic properties of dodecane/polystyrene systems

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Complex mechanical properties of dodecane/polystyrene systems were studied. The temperature and frequency dependence of the shear modulus was studied for various samples containing different amounts of dodecane. Addition of dodecane lowered the temperature at which mechanical transitions occurred and broadened the transition region. The modulus decreased with increasing dodecane content. The temperature and concentration dependences of the shift factor were determined by time–temperature and time–concentration superposition and analysed by a free-volume model and an entropy model. The concentration effect on the temperature-dependent shift factor was validated by an entropy model. The frequency-dependent complex moduli master curves experimentally determined were converted to a discrete relaxation time spectrum; subsequently, the time-dependent material function could be determined from the relaxation spectrum. The relaxation spectrum shifted significantly to shorter times with increasing concentration of dodecane.

(Keywords: dodecane/polystyrene system; complex moduli; shift factor)

INTRODUCTION

In the last few decades, studies[1–5] on the dynamic mechanical behaviour of polystyrene have focused on the analysis of the multiple transitions observed at fixed frequency to understand the origins of viscoelastic material transitions. Besides the α-transition attributed to the motion of $-CH_2-CH_2-$ segments of the main chain, secondary transitions attributed to one or more relaxation processes were reported. The β-transition was reported to be caused by the motion of some phenyl groups which possessed lower steric hindrance than the majority of phenyl groups. The origins of γ- and δ-transitions were reported to be the torsional motions of a number of $-CH_2-CH_2-$ units in the main chain formed by head-to-head coupling and oscillation or wagging of phenyl groups, respectively.

Several effects on the viscoelastic properties of polystyrene have been studied. Morgan and Nielsen[6] studied the effect of solvents on the cryogenic dynamic mechanical properties of polystyrene. The Young's modulus and mechanical damping of samples produced by incorporation of many organic liquids in polystyrene were measured. Van and Noel[7] studied the effect of chemical structure and thermal history on the β-transition of polystyrene and certain substituted polystyrenes. The β-transition depended on the thermal history of the sample, which would indicate that the final frozen structure in the glassy state was an important factor in the secondary transition. The chemical nature and position (*o*-, *m*-, and *p*-) of the substituent did not influence the location of the β-transition but only the peak height due to phenyl ring reorientation.

Boyer and co-workers[8–11] investigated the liquid–liquid transition which was possibly attributed to the onset of flow, changes in the chain entanglement and chain ends, or onset of motion of entire polymer chains occurring at temperatures higher than the glass transition temperature. Several effects on the liquid–liquid transition were studied such as plasticization[8], molecular weight[9] and dispersity[10]. The nature and the existence of a liquid–liquid transition has been controversially discussed[12,13].

Masuda *et al.*[14,15] studied the effect of the molecular weight distribution on the rheological properties in the terminal and rubbery zones by measuring blends of narrow distribution polystyrene in the molten state. The $\log G'$ *versus* $\log \omega$ curve for a binary blend having different molecular weights manifested a two-step rubbery plateau.

Schausberger[16] studied the nature of the relaxation-time spectrum of polystyrene blends. The presence of shorter molecules reduced the relaxation strength (a product of the weight fraction and the plateau modulus) of the large molecular component and the relaxation time of the polymeric system was considerably changed by blending.

Antonietti *et al.*[17] studied the effect of crosslinking on the polystyrene gels. The heterogeneity produced on a local scale by crosslinks caused the broadening of the transition zone. The mechanical relaxation of G' and G'' of the sample was shifted to lower frequency with respect to the curves of linear polystyrene owing to the increased glass transition temperature. In the plateau zone, the storage modulus was not affected by crosslinking.

Stadler *et al.*[18–20] studied the mechanical relaxation behaviour in the glass transition regime for polystyrene/poly[oxy(2,6-dimethyl-1,4-phenylene)] (PS/PPE) blends

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and poly(vinylmethylether)-*cross*-polystyrene semi-interpenetrating networks (PVME-*c*-PS-*semi*-IPN). In the case of PS/PPE blends where the temperature dependence of viscoelastic properties of PS/PPE blends for various compositions and various PPE chain lengths was analysed, the conditions of thermorheological simplicity were applied, but in the case of PVME-*c*-PS-*semi*-IPN, the different frequency dependence of the tan δ and E'', gave rise to the thermorheological complex behaviour.

Mechanical properties of polymeric solids are significantly affected by the presence of diluent. Understanding the penetrant dilution effect on the mechanical properties is of importance for polymeric materials used in structural applications exposed to various solvents. The objective of this research was to study the effect of dodecane on the viscoelastic properties of crosslinked polystyrene and to investigate the frequency dependence of the complex shear moduli as a function of temperature and concentration, resulting in the construction of complete viscoelastic master curves.

EXPERIMENTAL

Sample preparation

Crosslinked polystyrene was prepared by bulk polymerization. Styrene (Aldrich Chemical Co., Milwaukee, WI) was vacuum-distilled at 38°C and 15 mmHg (2 kPa). Divinylbenzene (Aldrich) was used as a crosslinking agent. Styrene monomer mixed with desired amounts of crosslinking agent at crosslinking ratios of X (= 0.005 mol DVB/mol styrene) was reacted in a convection oven at 125°C for 48 h and then in a vacuum oven at 125°C for 12 h to remove the unreacted monomer. Samples were prepared with dodecane at eight different dodecane concentrations of 0.0, 2.5, 5.0, 7.5, 10.0, 12.4, 16.8 and 20 wt% based on the total mixture.

Sample characterization

The physical properties of polystyrene and dodecane/polystyrene systems were characterized by various techniques. The chemical structure of the samples and the uniformity of dodecane concentration distribution throughout the sample were examined by transmission *FT*i.r. spectrometry (Model 1600, Perkin-Elmer, Norwalk, CT). The i.r. spectrum of the crosslinked polystyrene showed the same absorption bands as that of a standard polystyrene. The uniformity of the dodecane concentration distribution was investigated across the sample after reaching the equilibrium state, as the non-uniformity of dodecane concentration distribution might lead to erroneous results of physical and mechanical property measurements. Comparison of absorption bands in dodecane and polystyrene provided a quantitative analysis of the dodecane inside the polymer and information about the penetrant concentration distribution throughout the sample. The dodecane concentration distribution was uniform throughout the sample.

Glass transition temperatures were measured by differential scanning calorimetry (d.s.c.) (Model 910 DSC, Du Pont, Wilmington, DE) with a heat scanning rate of $10°\mathrm{C\,min^{-1}}$ at a nitrogen flow rate of $140\,\mathrm{ml\,min^{-1}}$. Thermogravimetric analysis (Model 951 TGA, Du Pont) was used to observe the thermal stability of samples. The heat scanning rate was $25°\mathrm{C\,min^{-1}}$ and the nitrogen flow rate was $160\,\mathrm{ml\,min^{-1}}$. The glass transition temperature and the onset point of degradation of undiluted polystyrene were 100.5°C and 250°C, respectively.

Sorption experiments on the effect of cyclohexane on polystyrene at 45°C were performed to determine the molecular weight between consecutive crosslinks, $\overline{M}_c$. The equilibrium swelling ratio, Q, and the equilibrium polymer volume fraction in the swollen polymer, υ_2, were determined from the values of weights of the unswollen polymer and the swollen polymer under the assumption that the mixing occurred without an appreciable change in the total volume of the system. The resulting value of $\overline{M}_c$ calculated from the Lucht–Peppas[21,22] equation was 5100. The value of $\overline{M}_c$ determined from the equilibrium swelling experiment was in good agreement with the value of molecular weight between crosslinks calculated from the change in the glass transition temperature between the crosslinked polystyrene and the linear polystyrene, $\overline{M}_{c,T_g}$[23,24].

Dynamic mechanical experiments

Samples were cut into rectangular shapes with typical dimensions 50 mm × 10 mm × 2.5 mm using a 16 in (40 cm) motorized band saw (Delta, Memphis, TN) and then smoothed with a fine file. Samples had uniform faces and square edges. Each sample was coated with silicone oil to prevent dodecane from releasing from the sample at high temperatures and then stored in a container for a week at room temperature.

Dynamic mechanical experiments were performed using a dynamic mechanical analyser (Model 983 DMA, Du Pont, Wilmington, DE) with a vertical clamp mode. The oscillation amplitude was 0.4 mm. For the study of temperature dependence of complex shear moduli, $G^*(\omega)$, the experiments were performed at 1 Hz with a heating rate of $3°\mathrm{C\,min^{-1}}$. Liquid nitrogen was used to provide cooling in measuring moduli below room temperature. For the study of frequency dependence of complex shear moduli, the experiments were performed by scanning frequency at isothermal conditions. Isotherms were measured from 30°C below glass transition temperature to 30°C above glass transition temperature at intervals of 3°C. The frequencies chosen for this experiment were 0.03, 0.05, 0.1, 0.2, 0.5, 1, 2 and 4 Hz.

Specific heat capacity determination

Heat capacity was determined by measuring the difference in calorimetric differential between the sample and blank runs by d.s.c. experiments. Quantities of 10 to 20 mg of samples were weighed to 0.1 mg, placed in aluminium sample holders while empty sample holders were used as references. For greater accuracy, the cell coefficient was measured by running a standard material, a sapphire standard of known specific heat capacity, under conditions identical to those of the sample. The standard specific heat capacity–temperature data for sapphire used in the present measurement had been determined by Ginnings and Furukawa[25]. The experimental accuracy was maximized by following the same procedure for each run, because heat capacity measurements are known to be affected by many parameters[26–31] including the specific experimental environment such as cooling rate, annealing time and pressure, as well as the material characteristics such as molecular weight, crosslinking and substitution, and tacticity. To identify the thermal history, the second heating run of the glass that had been formed under constant cooling rate, 10°C min^{-1}, was used. The heating rate was 10°C min^{-1} from a temperature well below the glass transition temperature.

RESULTS

Temperature dependence of shear moduli

Figure 1 shows the storage, G', and loss, G'', moduli for each system studied as a function of temperature at 1 Hz. The α-transition corresponding to the glassy to rubbery transition occurred at around 100°C for solvent-free polystyrene samples. The magnitude of the unrelaxed G' decreased slightly with increasing dodecane content. Presence of dodecane lowered the temperature at maximum loss peak height and broadened the transition peak due to the heterogeneity introduced in a local scale of macromolecular chains. In *Figure 2*, the temperature at the maximum loss peak was compared with the glass transition temperature determined from the PVT study[32] for dodecane/polystyrene systems. The glass transition temperature determined from the PVT experiment was 8°C lower than the temperature at the maximum loss peak. This reflects the shorter time-scale of the dynamic experiment.

Time–temperature superposition

It is already noted that time and temperature have essentially equivalent effects on the viscoelastic properties in that the shape of curves is similar and modulus values in each region are about equal. Because of the equivalent effect of time and temperature, the data taken at different temperatures can be superimposed on the data taken at a specified reference temperature, merely by shifting individual curves consecutively along the log ω axis about the reference temperature.

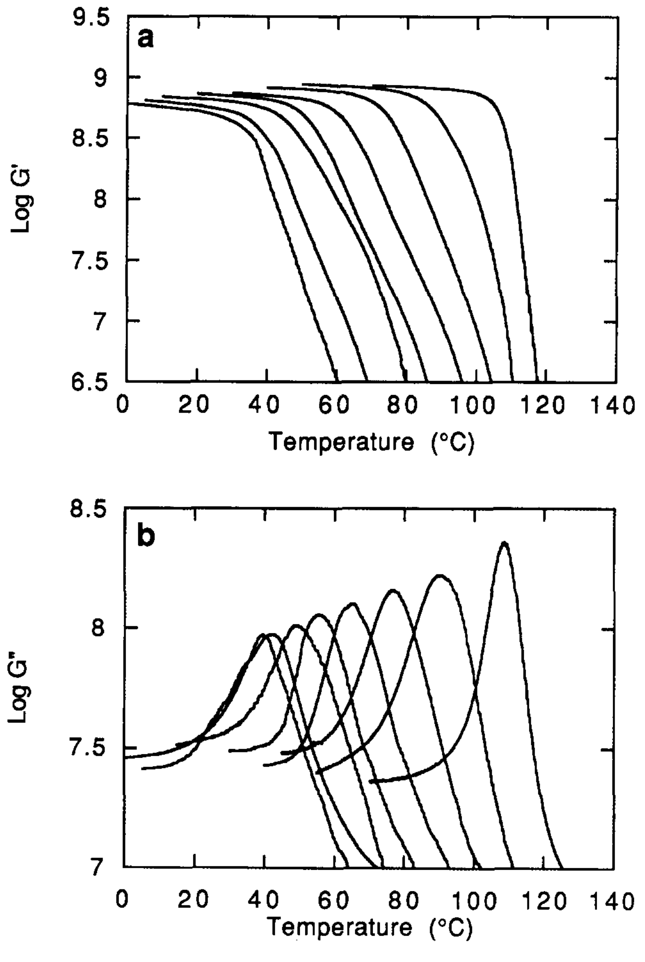

Figure 1 Shear storage (a) and loss (b) moduli of dodecane/polystyrene systems as a function of temperature at 1 Hz for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from right to left)

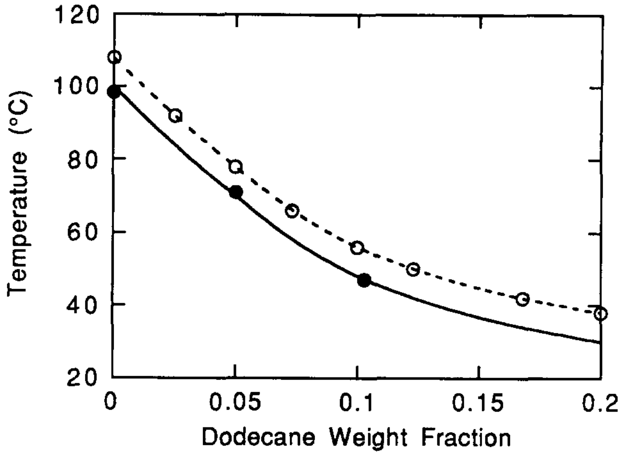

Figure 2 Glass transition temperature of dodecane/polystyrene systems as a function of dodecane weight fraction. (○) Temperature at the maximum loss peak from dynamic mechanical analysis measurement; (●) glass transition temperature from PVT measurements

$$G'[\omega, T] = G'[\omega a_T(T), T_R]$$

$$G''[\omega, T] = G''[\omega a_T(T), T_R] \qquad (1)$$

In equation (1), the temperature-dependent shifting function, a_T, can be obtained directly from the experimental curve by measuring the amount of shift along the log frequency scale necessary to match the curve. This parameter, a_T, is chosen as unity at reference temperature and is a function of temperature. The resulting complete response for either G' or G'' is known as the master curve.

Figure 3 shows the isotherms for undiluted polystyrene used for time–temperature superposition. Based on the glass transition temperature chosen from *Figure 2*, the isotherms were collected from $T_g - 30$°C to $T_g + 30$°C for each system. Above T_g, the isotherms were well superposed, but below T_g the superposition was somewhat arbitrary because the magnitude of G' or G'' did not change significantly. The time–temperature superposition to produce master curves of complex shear moduli for the samples including different compositions resulted in the associated log a_T shift factors as shown in *Figure 4*. The glass transition temperature of each system was chosen as the reference temperature to construct these master curves. The behaviour of the log a_T shift factor for dodecane-free polystyrene was in good agreement with the previous experimental results investigated by other researchers[33,34], but there was a slight deviation from the behaviour described by the universal Williams–Landel–Ferry (WLF) equation. From this comparison, the viscoelastic behaviour of the polystyrene sample used in this research was confirmed to be quite similar to those previously reported. The time–temperature superposition required that the same log a_T shift be applied to both the G' and G'' isotherms. *Figure 4b* shows the effect of concentration on the shift factor, log a_T, as a function of $T - T_0$. The shift factor of

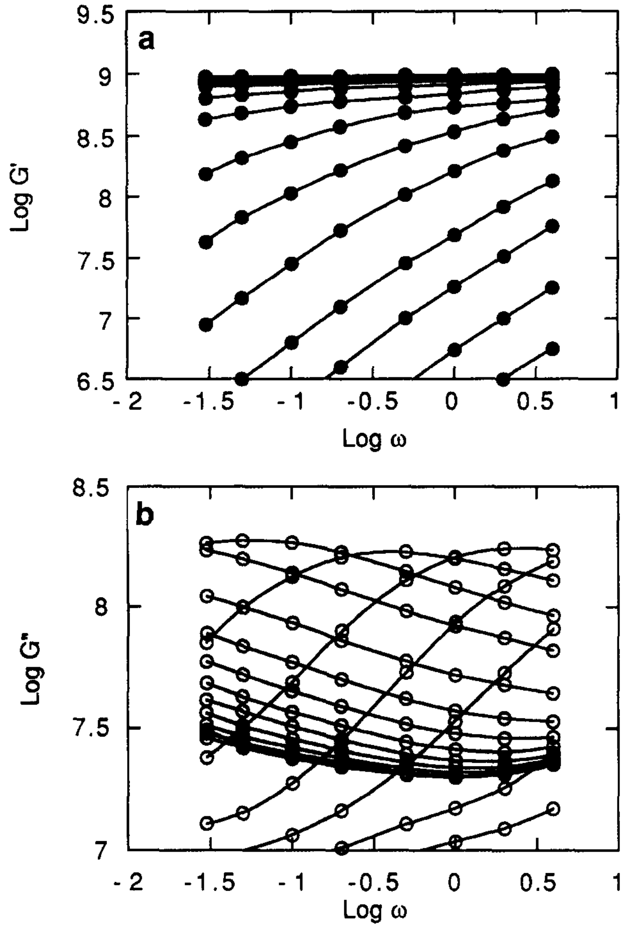

Figure 3 Isotherms of shear storage (a) and loss (b) moduli for undiluted polystyrene from $T_g-30°C$ to $T_g+30°C$ in intervals of 3°C

each system showed similar behaviour, but it seemed to have a slightly smaller shift for the less diluted sample. This observation will be discussed further below.

Time–concentration superposition

Figure 5 shows the master curves of dodecane/polystyrene systems as a function of dodecane concentration at a reference temperature of 100°C. The presence of dodecane displaced the frequency scale by several orders of magnitude. By analogy with the $\log a_T$ shift factor generated from the time–temperature superposition, the concentration dependence of the relaxation process, a_C, defined as the ratio of monomeric friction coefficient in the presence of diluent to that in the undiluted polymer, could be determined from the displacement along the logarithmic frequency axis for different concentrations.

Time–temperature superposition and time–concentration superposition produced master curves for complex moduli at the reference temperature of 100°C and at the reference concentration of zero dodecane fraction as shown in *Figure 6*. Similarly to *Figure 1*, the presence of dodecane broadened the transition zone slightly and reduced the maximum loss peak height. In *Figure 7*, the associated concentration-dependent shift factor, $\log a_C$, was plotted against dodecane weight fraction for a reference concentration of zero dodecane weight fraction.

Free volume-based shift factor

The free-volume model[35,36] was applied to describe the temperature and concentration dependence of shift factors for the dodecane/polystyrene system. The free-volume $\log a_T$ model depends on the fractional free volume, f, according to the following equation[37]:

$$\log a_T = \frac{B}{2.303}\left(\frac{1}{f} - \frac{1}{f_0}\right) \qquad (2)$$

where B is a material parameter and f_0 is the fractional free volume at temperature T_0.

The fractional free volume was determined from the actual PVT data[32] and the occupied volume data under the assumption that the additivity of occupied volume was applicable to the present dodecane/polystyrene system as had been applied for the polymer blend system[38].

The occupied volumes of pure components, dodecane and undiluted polystyrene could be determined, when either the crystalline volume or the van der Waals' volume of each component was set equal to the occupied volume. The crystalline volume of dodecane was obtained from the experimental volume–temperature data[39] and that of polystyrene from the density[40] determined at room temperature. The crystalline volume of each component experimentally determined was extrapolated to the temperature of interest, under the assumption that the thermal expansion coefficient of a polystyrene crystal was the same as that of the polystyrene glass[40]. The values

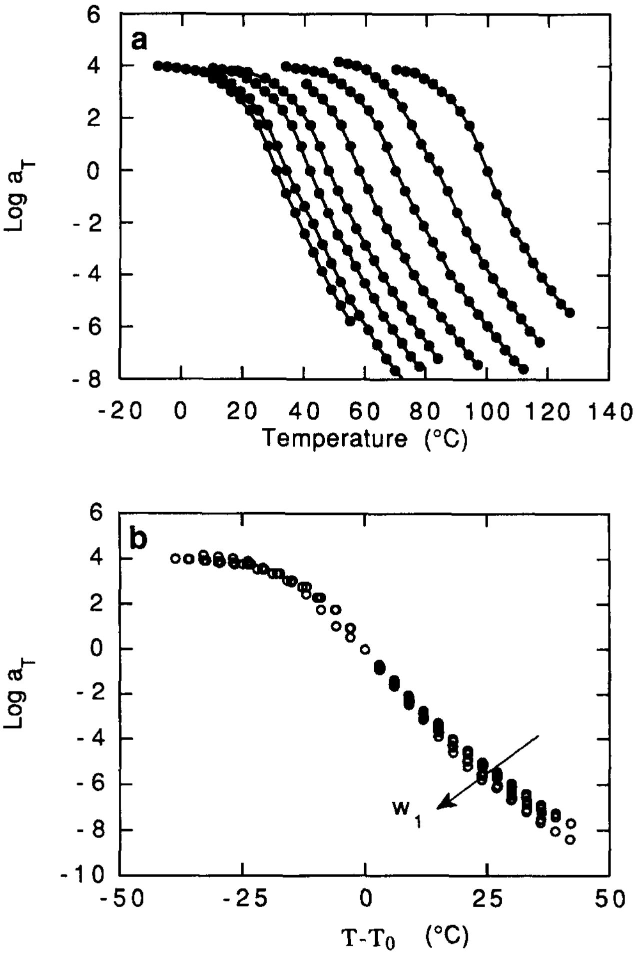

Figure 4 Temperature-dependent shift factors, $\log a_T$, for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from right to left), determined (a) with respect to the reference temperature of glass transition temperature of each system and (b) as a function of $T-T_0$

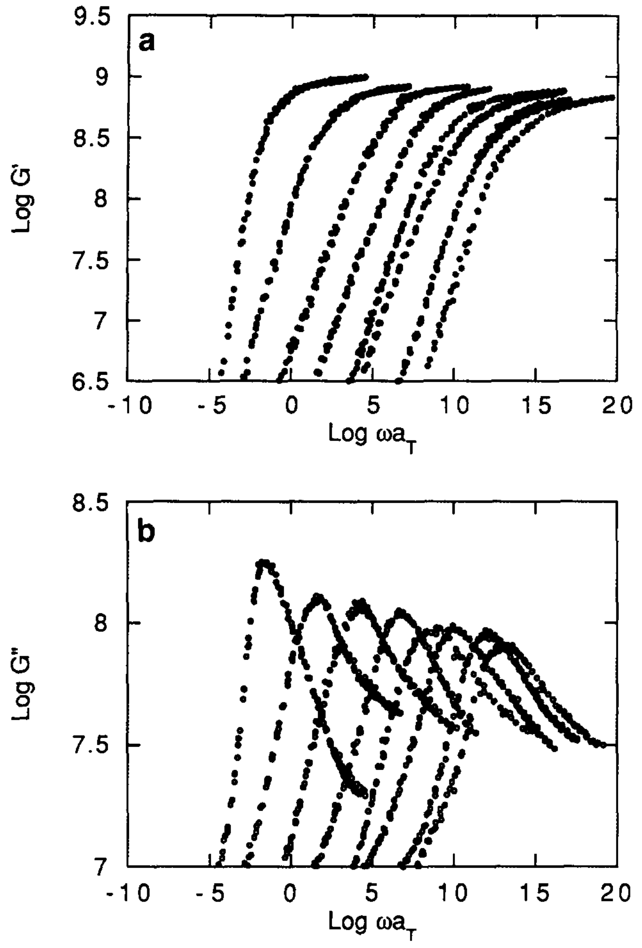

Figure 5 Master curves of shear storage (a) and loss (b) moduli of dodecane/polystyrene systems for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from left to right), at a reference temperature of 100°C

of the van der Waals' volumes of dodecane and pure polystyrene were determined to be 0.73 and 0.605 cm^3 g^{-1}, respectively, by applying group contribution methods[41,42]. The actual volume and the occupied volume based on either the crystalline volume or the van der Waals' volume as a function of temperature are presented in *Figure 8*.

The fractional free volume of each system could be determined by subtracting the additive occupied volume calculated from the two pure components from the actual volume experimentally determined, and is shown in *Figure 9*. In the temperature range above the glass transition temperature, the fractional free volume increased linearly with temperature. The parameter, B, describing the $\log a_T$ free-volume model for the present system was determined by plotting experimentally determined $\log a_T$ against $1/f - 1/f_0$ calculated as shown in *Figure 10*. In the temperature range above the glass transition temperature and the concentration range of experimental data concerned, the material parameter, B, seemed to be concentration-independent. The temperature-dependent shift factor, $\log a_T$, could be described well by the free-volume model with the same value of B as shown in *Figure 11*.

The free-volume model was also applied to predict the concentration-dependent shift factor, $\log a_C$, described by the following equation:

$$\log a_C = \frac{B'}{2.303}\left(\frac{1}{f_C} - \frac{1}{f_2}\right) \tag{3}$$

where f_C is the fractional free volume at concentration C, and f_2 that of the undiluted polymer. The application of Fujita and Kishimoto's hypothesis[43,44] of a linear dependence of f_C on w_1 made it possible to determine the parameter B' in the concentration-dependent shift factor involved in equation (3). The parameter B' could be determined by best fitting of $\log a_C$ experimentally determined at 100°C to $1/f_C - 1/f_2$ calculated as shown in *Figure 12*. The values of B' determined from the two different approaches, i.e. the crystalline and van der Waals' occupied volume basis, were determined to be 3.161 and 75 with the known values of f_2 ($=0.075$ and 0.38) and β ($=0.195$ and 0.19), respectively. The parameter β denotes the slope of linear correlation between f_C and the dodecane fraction w_1.

Entropy-based shift factor

An alternative $\log a_T$ shift function proposed by Adam and Gibbs[45] was applied to the present system. In the Adam–Gibbs entropy-based shift factor, the relaxation rate of the polymeric material is proportional to the total number of configurations available to the polymer. The configurational entropy can be calculated from the experimental heat capacity, C_p, resulting in the following description of the shift factor.

$$\log a_T = B''\left(\frac{1}{\eta T} - \frac{1}{\eta_0 T_0}\right)$$

$$\eta = \eta_0 + \int_{T_0}^{T} \frac{\Delta C_p}{T}\,\mathrm{d}T \tag{4}$$

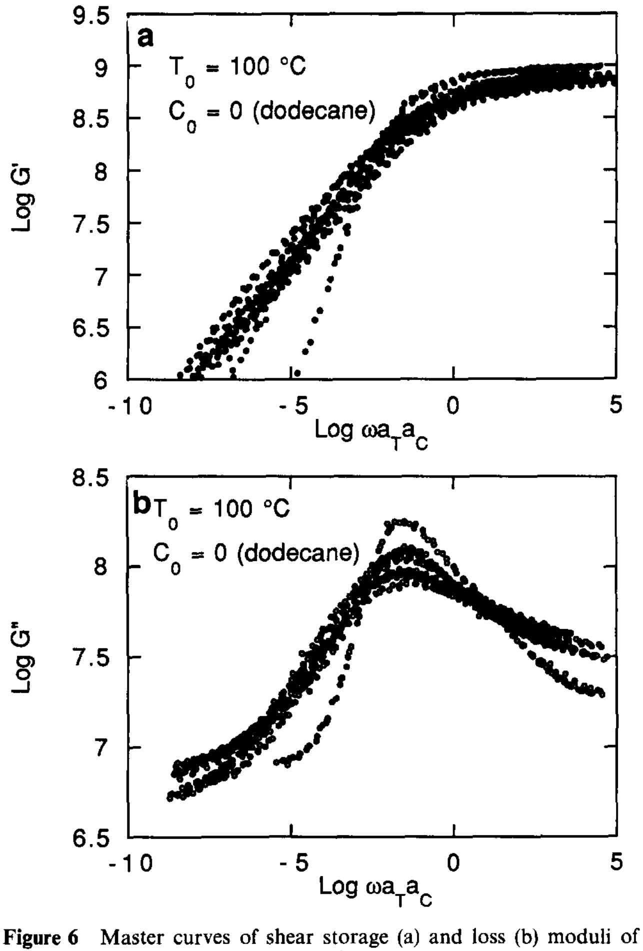

Figure 6 Master curves of shear storage (a) and loss (b) moduli of dodecane/polystyrene systems at a reference temperature of 100°C and a reference concentration of zero dodecane weight fraction

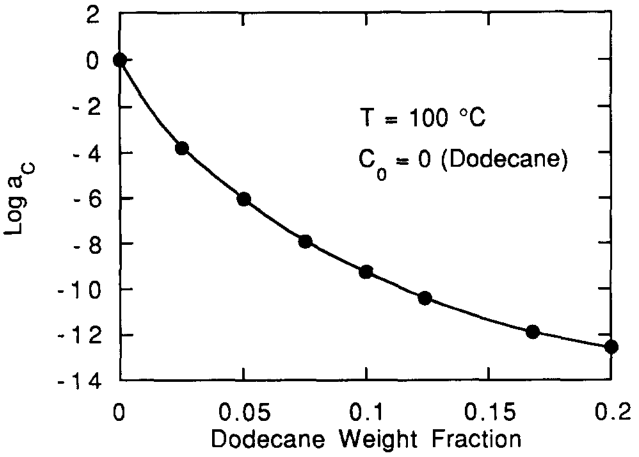

Figure 7 Concentration-dependent shift factor, log a_C, determined for a reference concentration of zero dodecane weight fraction at 100°C

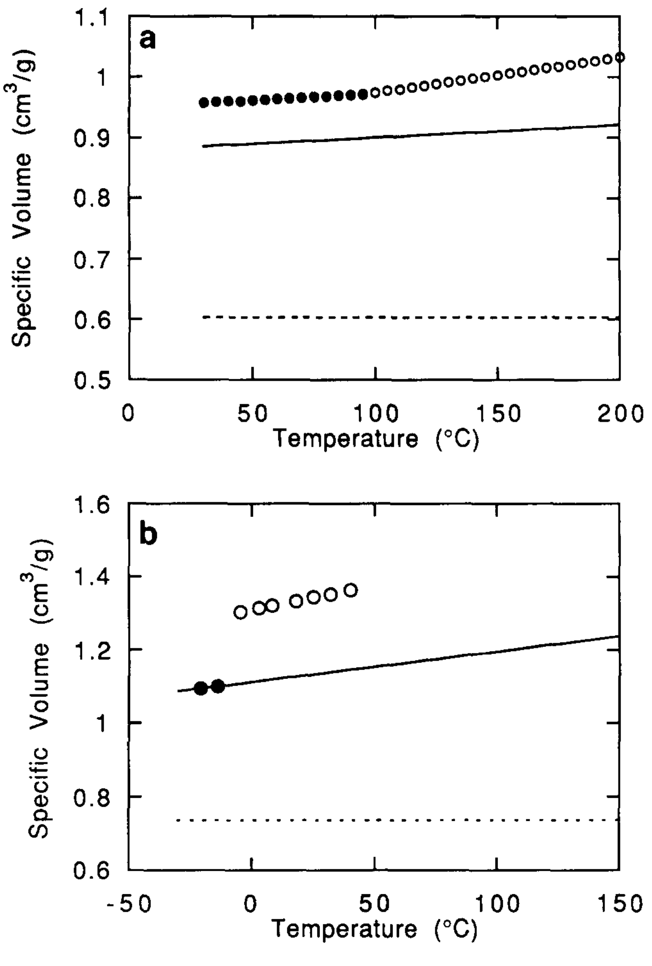

Figure 8 Actual specific volume, crystalline volume (——) and van der Waals' volume (---) as a function of temperature for (a) pure polystyrene and (b) pure dodecane. (a) ●, glassy; ○, rubbery regions of polystyrene; (b) ●, crystal; ○, melt states of dodecane

Here, B'' is the material constant, η is the configurational entropy at temperature T and η_0 is the configurational entropy at a reference temperature, T_0. The glass transition temperature at atmospheric pressure was taken as a reference state in this study, and ΔC_p is $C_{pl}-C_{pg}$, where C_{pl} and C_{pg} are the isobaric heat capacities of the rubbery and glassy states, respectively. Equation (4) is based on the idea that C_{pg} is a measure of the vibrational contribution to specific heat and that the difference between C_{pl} and C_{pg} results from the configurational molecular rearrangement in the liquid.

The heat capacity of each system at atmospheric pressure determined from d.s.c. experiments is shown in *Figure 13*. In the glassy region, the heat capacity was fairly well described by addition of heat capacities of pure components, but in the rubbery region, the applicability of additivity was hard to prove, because the reference data for dodecane heat capacity[39] were available only in the temperature range to 50°C in this study. As a reference, the heat capacities outside the glass transition region were found to be additive for copolymer systems[27]. Heat capacity of undiluted polystyrene measured in this research was in accordance with the reference data reported[28-31,46].

The material constant, B'', and reference entropy, η_0, were determined by relating the entropy-based shift function described in equation (4) to the experimentally measured shift function, log a_T, shown in *Figure 4a*. As shown in *Figure 14*, plotting log a_T against $1/\eta T - 1/\eta_0 T_0$ for a series of assumed η_0, can determine the reference entropy, η_0, by selecting a curve which gives the best linear correlation coefficient, as well as the material parameter, B'', from the slope of that curve. The values of η_0 and B'' determined from this analysis for

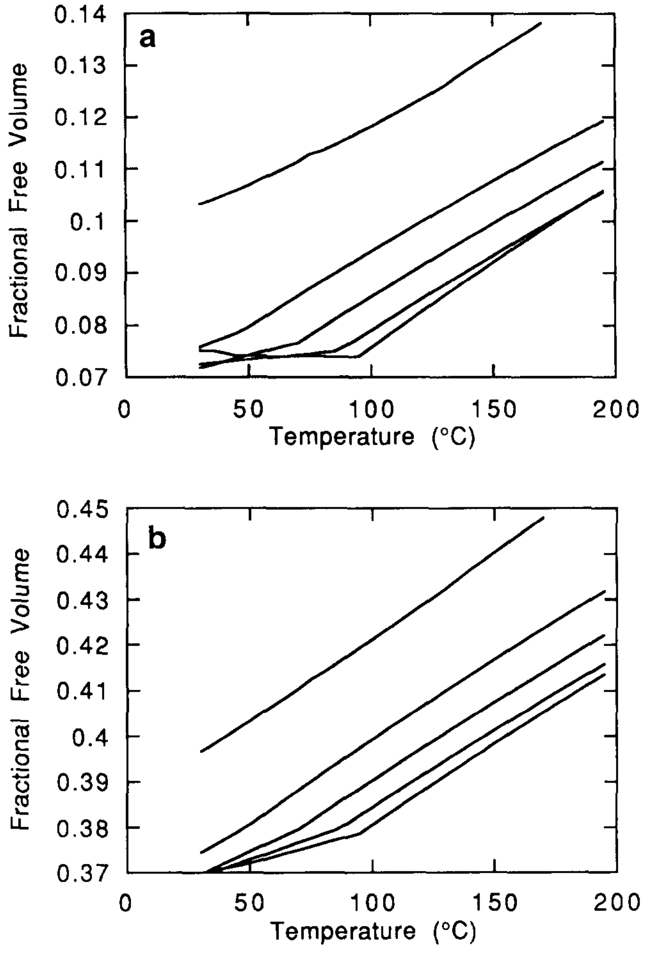

Figure 9 Fractional free volume as a function of temperature for samples of varying compositions of 0, 0.025, 0.05, 0.1 and 0.2 weight fractions of dodecane (curves from bottom to top), based on the two occupied volume theories, (a) crystalline volume and (b) van der Waals' volume

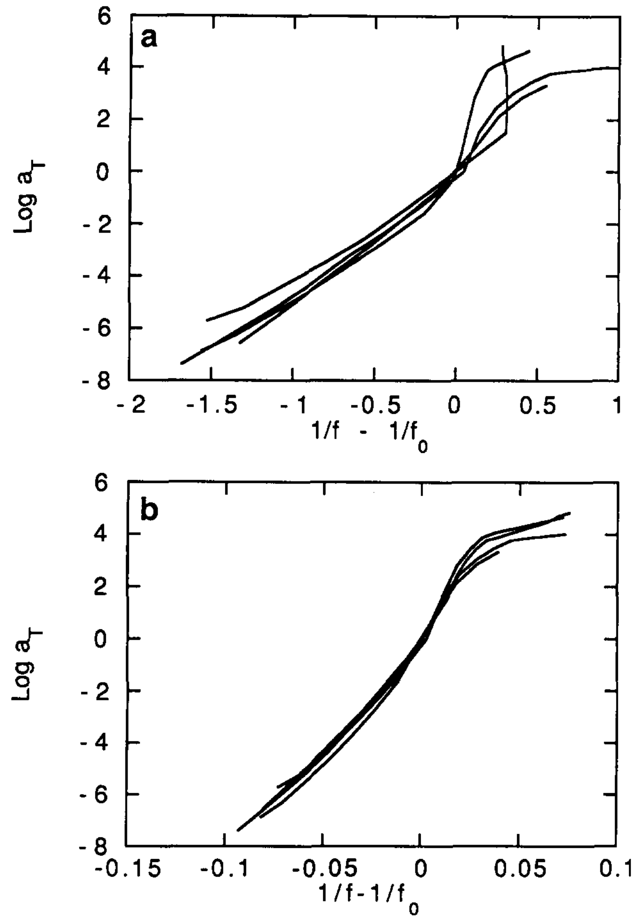

Figure 10 The $\log a_T$ experimentally determined as a function of $1/f - 1/f_0$ calculated from the free-volume model based on the two occupied volume theories, (a) crystalline volume and (b) van der Waals' volume for samples of varying compositions of 0, 0.025, 0.05 and 0.1 weight fractions of dodecane (curves from right to left)

the dodecane-free polystyrene were $0.06349\ \mathrm{J\,g^{-1}\,K^{-1}}$ and $423.21\ \mathrm{J\,g^{-1}}$, respectively.

With the known values of reference entropy, η_0, and heat capacity, the configurational entropy for each system could be computed using equation (4) and the results are shown in *Figure 15*. In this calculation, the reference entropy for each system was assumed constant, based on the two following postulates: (1) the configurational entropy is zero at the thermodynamically defined second-order transition temperature, T_2, which occurs below the glass transition temperature of each system; and (2) the variation in the difference between the experimentally determined T_g and the theoretically predicted T_2 as a function of molecular weight, plasticizer concentration, copolymer composition and degree of crosslinking is negligible[45]. In *Figure 15*, the configurational entropy for the undiluted polystyrene sample decreased with decreasing temperature and vanished at $T_2 = 317$ K, below which the configurational entropy remained zero rather than going to meaningless negative values. The temperature difference of $T_g - T_2 = 56°\mathrm{C}$ was close to the previously reported value of 61°C[45].

Rearrangement of equation (4) showed the temperature and concentration contribution to entropy:

$$\eta(C, T) = \eta_0(C=0, T=373\ \mathrm{K}) + \Delta\eta_0(C, T=373\ \mathrm{K}) + \int_{T_0}^{T} \frac{\Delta C_p(C, T)}{T}\,\mathrm{d}T \qquad (5)$$

The first term in the right-hand side of equation (5) denotes the entropy at the reference condition, in this case, the glass transition temperature (373 K) of undiluted polystyrene ($C=0$), the second term the contribution of dodecane concentration to the shift factor of the sample at the reference condition, and the third term the contribution of temperature to the shift factor of the sample at the reference condition.

The computed shift function based on the entropy model is shown in *Figure 16*. The experimentally measured shift factor and entropy-based shift factor were in fairly good agreement. The concentration dependence on the shift factor decreases with increasing temperature as shown in *Figure 17* in which the entropy-based shift factor is shown as a function of concentration for different temperatures. It is expected that at very high temperatures there is no concentration effect on the shift factor. The concentration effect on the temperature-dependent shift factor, $\log a_T$, was validated by consideration of concentration effect on the temperature-dependent specific heat for each system. The temperature dependence of entropy could be rearranged into the following two terms:

$$\int_{T_0}^{T} \frac{\Delta C_p(C, T)}{T}\,\mathrm{d}T = \int_{T_0}^{T} \frac{\Delta C_p(C=0, T)}{T}\,\mathrm{d}T + \int_{T_0}^{T} \left[\frac{\Delta C_p(C, T)}{T} - \frac{\Delta C_p(C=0, T)}{T}\right]\mathrm{d}T \qquad (6)$$

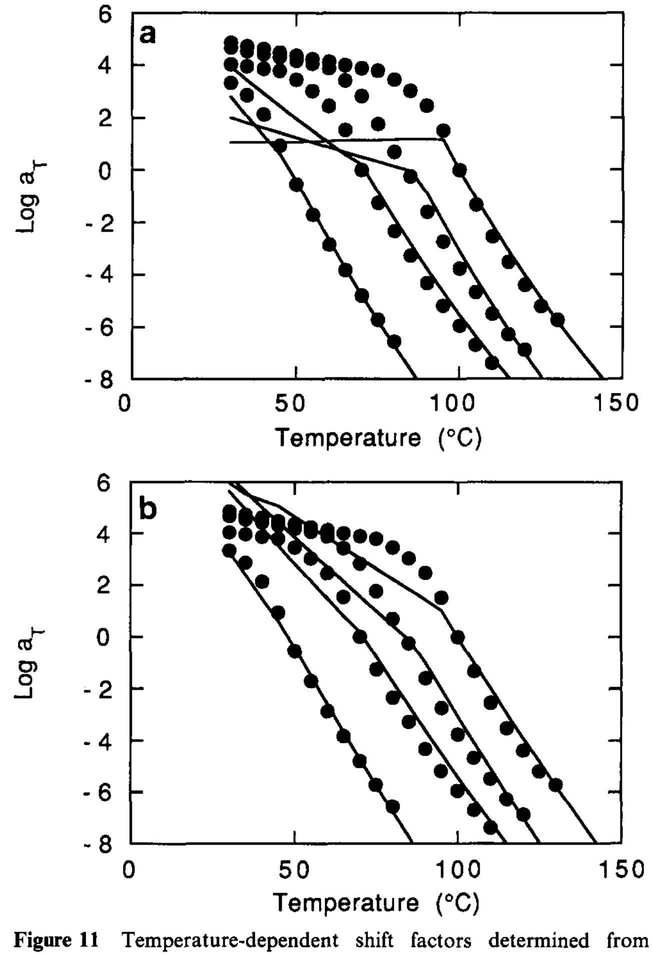

Figure 11 Temperature-dependent shift factors determined from experiments (●) and from free-volume model (——) based on the two occupied volume theories, (a) crystalline volume and (b) van der Waals' volume for samples of varying compositions of 0, 0.025, 0.05 and 0.1 weight fractions of dodecane (curves from right to left)

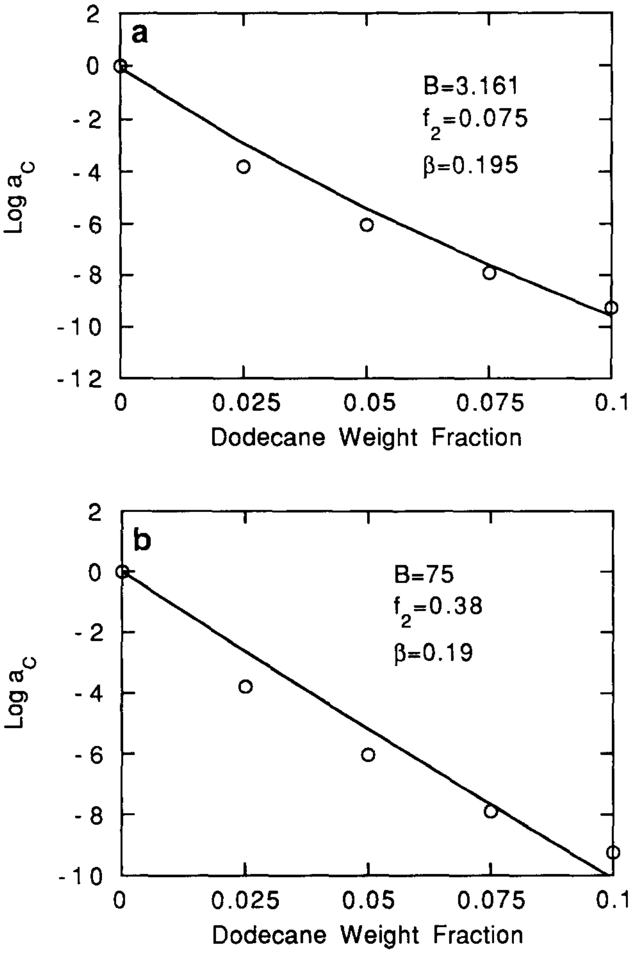

Figure 12 Concentration-dependent shift factor determined from experiments (○) at 100°C and from free-volume model (——) based on the two occupied volume theories, (a) crystalline volume and (b) van der Waals' volume

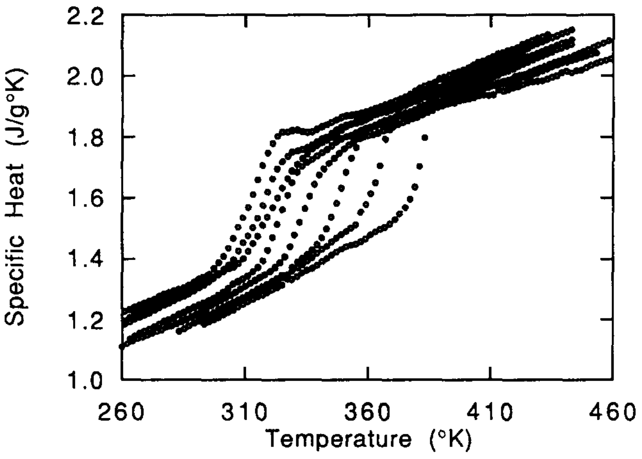

Figure 13 Heat capacities of dodecane/polystyrene systems as a function of temperature for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from bottom to top)

Here, the first term of the right-hand side of equation (6) denotes the temperature dependence of the shift factor for undiluted polymer ($C=0$) and the second term the concentration contribution to the temperature-dependent shift factor, resulting in the different shape of

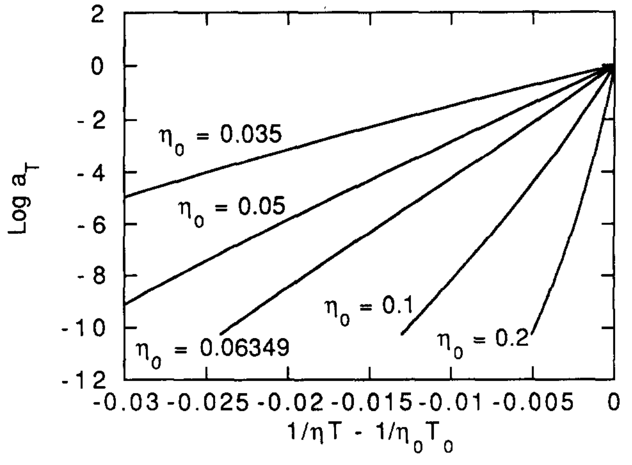

Figure 14 Correlation between $\log a_T$ determined from experiments and $1/\eta T - 1/\eta_0 T_0$ determined from entropy model for a series of assumed η_0

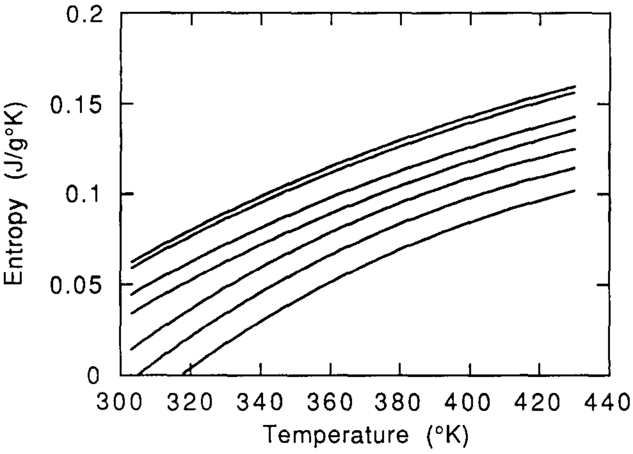

Figure 15 Configurational entropies of dodecane/polystyrene systems as a function of temperature for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from bottom to top)

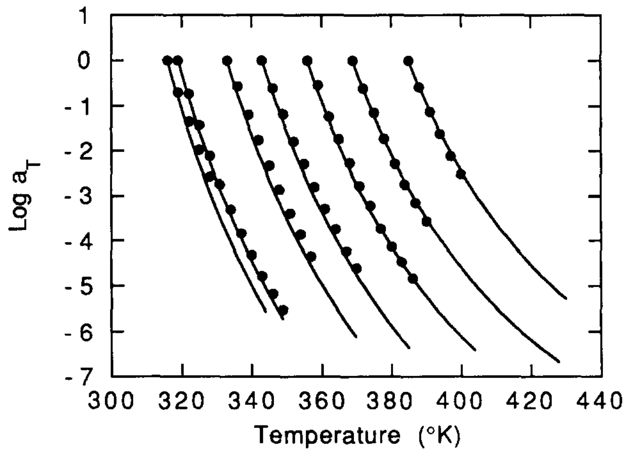

Figure 16 Temperature-dependent shift factors of dodecane/polystyrene systems determined from experiments (●) and from configurational entropy model (——) for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.168 and 0.2 weight fractions of dodecane (curves from right to left)

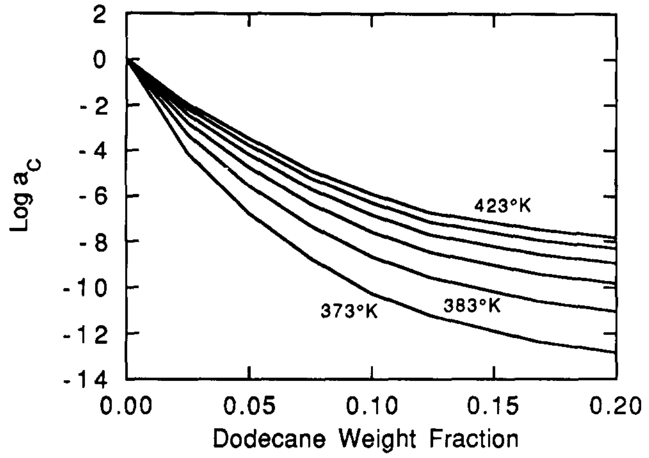

Figure 17 Entropy-based shift factors of dodecane/polystyrene systems as a function of dodecane weight fraction for samples of varying temperatures from 373 to 423 K at 10 K intervals (curves from bottom to top)

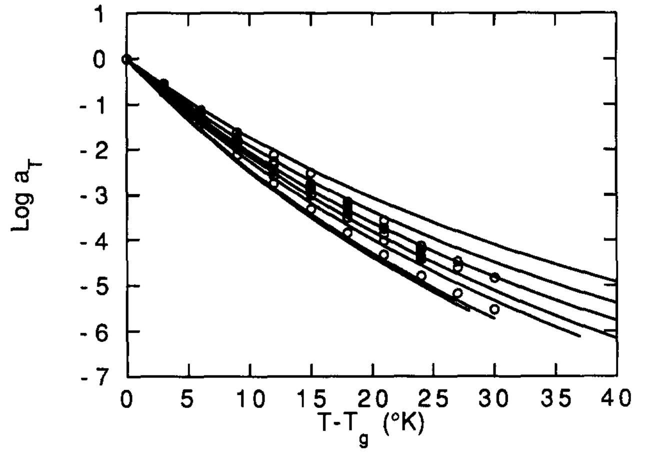

Figure 18 The log a_T of dodecane/polystyrene systems as a function of $T-T_0$ determined from experiments (○) and from the configurational entropy model (——) for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane

log a_T *versus* $T-T_g$ as shown in *Figure 4b*. Comparison of the log a_T *versus* $T-T_g$ relation determined from the experiments and from the entropy model is shown in *Figure 18*. Qualitatively, the concentration effect on the temperature-dependent shift factor was well described by the Adam–Gibbs entropy theory.

Discrete relaxation moduli

The dynamic moduli $G'(\omega)$ and $G''(\omega)$ experimentally determined were converted into a discrete relaxation modulus $G(t)$ using a regularized quadratic programming (RQP) provided by our group[47]. The ROP simultaneously determined a discrete relaxation spectrum from well separated $G'(\omega)$ and $G''(\omega)$ data.

The recalculated moduli, G' and G'', from the discrete relaxation spectra were well fitted to the experimentally determined moduli for undiluted polystyrene around the transition zone. *Figure 19* shows the relaxation spectra for each system at the reference temperature of 100°C. The relaxation spectra shifted significantly to shorter times with increasing dodecane concentration. If the shift factor, log a_C, is applied to this system, each system can be shifted to the reference relaxation spectrum of dodecane-free polystyrene.

Figure 20 shows the shear modulus as a function of time inverted from $G'(\omega)$ and $G''(\omega)$. The dodecane dilution effect on this relationship was as same as that on the relaxation spectra.

DISCUSSION

The presence of dodecane strongly affected the mechanical properties of dodecane/polystyrene systems. In particular, the transition temperature decreased significantly with increasing dodecane content. The relaxation time shifted significantly to lower values with increasing dodecane content. The plasticization of these dynamic viscoelastic properties is typically attributed to the greater mobility in the macromolecular chains with the addition of dodecane. This can be explained using the apparent activation energies for the transition shift functions which decrease with increasing dodecane content[48]. The fact that interchain mobility barriers are disrupted in the presence of dodecane, allowing increasing penetrant chain mobility, provides decreasing activation energy.

The determination of material parameters, B and f_0, in the free-volume shift factor model is very dependent upon the occupied volume basis which cannot be determined by direct measurement. Generally, the occupied volume is defined as either the zero point

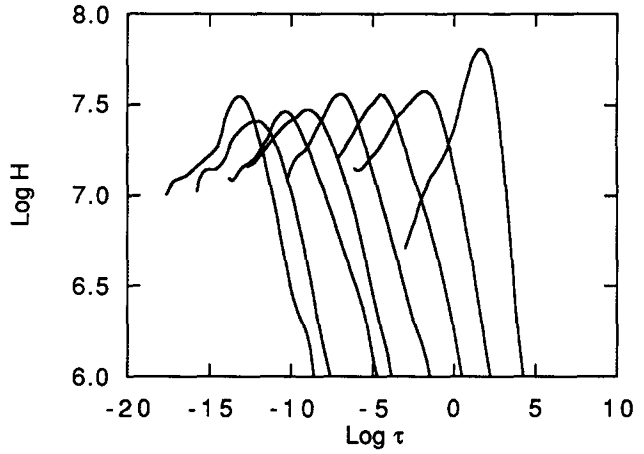

Figure 19 Discrete relaxation spectra of dodecane/polystyrene systems determined at 100°C for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from right to left)

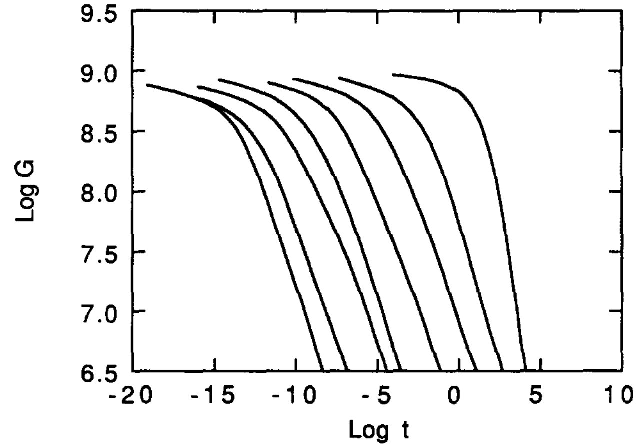

Figure 20 Shear modulus of dodecane/polystyrene systems at 100°C as a function of time for samples of varying compositions of 0, 0.025, 0.05, 0.075, 0.1, 0.124, 0.168 and 0.2 weight fractions of dodecane (curves from right to left)

volume (V(0 K)) or the volume involving the zero point volume and the interstitial free volume caused by the anharmonic vibrational part of molecular motion[37,49]. The introduction of either crystalline volume or van der Waals' volume as an occupied volume is based upon the fact that the zero point volume is possibly determined by extrapolation of crystalline substances to 0 K[50,51] and the zero point volume is closely related to the van der Waals' volume[41]. The parameter, B, is sometimes set equal to a value of 1 for simplicity[38]. Although a free-volume model was able to describe the shift factor of the present system, it failed to provide a qualitative or quantitative description of the concentration effect on the temperature-dependent shift factor.

Since the configurational entropy, η, is theoretically defined as the difference in the entropy between the liquid and crystalline states at the same temperature, the precise calculation of η requires the heat capacity difference, $\Delta C_p = C_{pl} - C_{pc}$ instead of $\Delta C_p = C_{pl} - C_{pg}$. It was observed from the experimental results of several researchers[29–31] that glass and crystal had almost the same heat capacity and the crystallinity dependence was observed only above the glass transition temperature. Thus, it was possible to replace C_{pc} by C_{pg} in the calculation of configurational entropy.

Actually, a fraction of the ΔC_p assumed to describe the measure of the molecular rearrangements in the liquid may possibly arise from anharmonic vibrational relaxations[52–54]. Because these processes are relevant to the cooperative rearrangement involved in flow, their contribution to ΔC_p should be subtracted to calculate precise configurational entropy, η. In *Figures 13* and *14*, the deviation between the actual shift factor and the entropy-based shift factor possibly arises from the inappropriate use of the total ΔC_p without correction for the anharmonic contributions or experimental inaccuracy. The Adam–Gibbs entropy model is known to be more successful than free-volume theory in accounting for the pressure dependence of the viscoelastic behaviour. The free volume does not represent a real molecular volume and not only inter- and intramolecular interaction but the topology of molecular packing in the amorphous phase should be understood. Thus in order to improve analysis of the relaxation phenomena, especially as related to the shift function, one should consider the quasi-static properties such as T_g and specific heat of the desired materials. Qualitatively, the concentration effect on the temperature-dependent shift factor could be fairly well described by the Adam–Gibbs entropy model, but the quantitative description of the concentration effect on this shift factor was not easily confirmed owing to the level of experimental accuracy.

Besides the free-volume and entropy models, several models have been proposed to describe the $\log a_T$ shift factor, including a model[55] reformulated from the Eyring's rate theory and Cohen and Turnbull's free-volume theory, and models based on the concept of fictive temperature proposed by Tool[56] and Narayanaswamy[57], and proposed by Mazurin *et al.*[58].

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