the nature of the LE–LC transition is a van der Waals type rather than a fluid to crystal type of transition.

Conclusions

The π–A isotherms of the fully quaternized PVP monolayers spread at the air–aqueous KBr solution interface include the flat portion corresponding to LE–LC transition even with changing temperature. They show a remarkable temperature dependency and condense with decreasing temperature. Application of the two-dimensional Clausius–Clapeyron equation gives heats and entropies associated with the transition that are relatively smaller than those of uncharged polymer monolayers due to the freedom of motion of pyridinium ring adsorbed at the air–aqueous KBr solution interface. Thus, the nature of the LE–LC transition of the quarternized PVP monolayers is not simply related to a fluid to crystal transition.

Registry No. PVPC6, 107455-36-7; PVPC8, 74343-05-8; PVPC12, 75503-70-7; KBr, 7758-02-3.

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Detection of T_{ll} in Styrene–Ethyl Acrylate Random Copolymers by Differential Scanning Calorimetry and Dynamic Mechanical Analysis

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ABSTRACT: There is a paucity of planned experimental investigations concerning the liquid–liquid transition/relaxation (T_{ll}) in random copolymers. A styrene–ethyl acrylate (S/EA) series, containing both homopolymers and seven copolymers of varying composition, has been prepared by free radical methods and studied by both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The T_{ll} and T_g transitions were reliably and reproducibly detected by both methods, varied smoothly as a function of copolymer composition, and obeyed the relationship $T_{ll} = 1.2T_g$. The observed data are discussed within the framework of the Lobanov–Frenkel model for molecular events occurring at T_{ll}.

Introduction

The existence of a discrete molecular transition and/or relaxation occurring in polymers above the glass transition (T_g) was predicted by Ueberreiter in 1943[1] and was formalized and designated as the liquid–liquid transition (T_{ll}) by Boyer in 1963.[2] In 1966 it was postulated that T_{ll} was a general transition associated with the amorphous state of polymers and it was shown that there were already considerable published data (thermal, spectroscopic, and dynamic mechanical) demonstrating this phenomenon in atactic polystyrene.[3] In the ensuing 20 years, studies of T_{ll} have generated an extensive set of experimental observations both supporting and criticizing the T_{ll} phenomenon. Two review articles summarize both the experimental evidence and theoretical arguments on both sides of the controversy.[4,5] It should also be noted that some of the various possible liquid state transitions/relaxations—including T_f (fusion–flow temperature), T_{ll} (an intermolecular process), and $T_{1\rho}$ (an intramolecular process, formerly $T_{ll'}$)—have been compared and contrasted.[5]

The nature of the molecular event(s) occurring at T_{ll} seems to be most consistent with the hypothesis of Frenkel[6,7] that macromolecules in the liquid state above T_g (but below T_{ll}) exhibit both gaslike random coil behavior of the entire macromolecule and liquidlike behavior characterized by segment–segment contacts or interactions (either between chains or within the same chain). As the temperature increases to T_{ll} the attractive forces (primarily enthalpic) are overcome and "segmental melting" occurs. The gain in entropy of the system as the individual chains are freed from segmental restraints provides the driving force for the transition/relaxation. In contrast to many of the published reports, the present study is the first one intentionally designed to investigate the T_{ll} relaxation in random *copolymers* and is directed toward answering four questions:

a. Does the T_{ll} relaxation occur in random copolymers?

b. Can this transition be detected by more than one type of experimental method?

c. Does T_{ll} in such a system vary in a smooth and predictable manner as the copolymer composition is varied?

d. Is there a systematic, well-defined relationship between T_g and T_{ll} in random copolymers?

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The results to be reported here,[8,9] on the examination of a series of styrene–ethyl acrylate (S/EA) random copolymers by both differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), provide answers to these questions and represent the first attempt to overcome the paucity of data concerning the T_{ll} relaxation in random copolymers.

DSC Evidence for T_{ll}. Gillham and co-workers have accumulated considerable data on the T_{ll} relaxation in polystyrene by both torsional braid analysis (TBA) and DSC.[10-12] In addition, the DSC technique has been employed to follow the molecular weight dependence of T_g and T_{ll} for atactic polystyrene (PS),[13-17] the effect of tacticity on both transitions in poly(methyl methacrylate) (PMMA),[18] the molecular weight dependence of these transitions in atactic PMMA,[19] and the effect of structure on T_g and T_{ll} in a series of poly(alkyl acrylates) and poly(alkyl methacrylates).[20] Some of these DSC results, notably for atactic PS, have been disputed[21] and/or ascribed to artifacts,[22] although the latter conclusion has been shown to be erroneous.[17,23]

DMA Evidence for T_{ll}. Dynamic mechanical analysis (DMA) has been, and continues to be, a standard technique for determining the dynamic mechanical properties of polymeric materials.[24,25] A concise summary of the comparative features of several common mechanical spectrometers and a discussion of the existing literature data on detection of T_{ll} by DMA have been presented.[26] The nature of these techniques does, however, present special problems when attempting to study transitions/relaxations in the liquid state, i.e., above T_g in amorphous materials or above T_m in semicrystalline polymers. The high mobility and low modulus exhibited by materials in these temperature regimes present the major difficulty. Recently, as part of a study describing a new technique for extending the useful range of DMA experiments, a review of existing DMA methods appeared.[27] That work critically examined techniques that have been described to overcome the problems mentioned above and presented a new technique—use of a perforated shim stock support in conjunction with the Du Pont 981 dynamic mechanical analyzer—that increases the useful upper temperature range of DMA studies of polymers by more than 100 °C.

The use of a solid metal support for dynamic mechanical methods based on flexural deformation was first proposed by Starkweather and Giri.[28] Keinath and Boyer demonstrated the utility of a perforated shim stock support for studying the liquid range of polymers[27] and extended the so-called "holey shim stock" technique to a variety of polymeric systems including blends.[29] Usually, loss peaks ascribed to T_{ll} were detected in both heating and cooling modes. For the current study, the most pertinent result was the detection of T_{ll} in a styrene–ethyl acrylate random copolymer; similar results were observed with a styrene–acrylonitrile random copolymer.[27]

Finally, Keinath[30] has studied (by unsupported DMA methods) a series of binary blends of poly(dimethylphenylene oxide) with various poly(alkyl methacrylates). Six of the eight blends studied exhibited well-defined T_{ll}s at the expected temperatures; the blend of PMMA gave a T_{ll}/T_g ratio lower than expected, and no T_{ll} was detected in the blend of poly(*tert*-butyl methacrylate). These results were discussed in terms of the mutual compatibility or incompatibility of the two phases.

T_{ll} in Random Copolymers. Detection of T_{ll} in random copolymers has a very limited scope. The random copolymer that has been most extensively studied is styrene–butadiene rubber (SBR). A critical analysis of much of the existing literature on this copolymer (including various dynamic mechanical methods and high precision adiabatic calorimetry data on four National Bureau of Standards SBRs) has appeared.[4] This analysis concludes that the T_{ll} transition does, in fact, appear in SBRs of varying styrene content (ranging from 9% to 43%) although its presence was not noted by the original authors. Plots of both T_{ll} and T_g vs. styrene content are parallel throughout the range represented and T_{ll}/T_g ratios are consistently about 1.20.

There are isolated examples suggesting the presence of T_{ll} in other random copolymers; these have been discussed in a recent review article.[5] A clear example of the detection and assignment of T_{ll} in butadiene–acrylonitrile (BAN) copolymers is provided by the TBA results of Manzione and Gillham[31] on a series of low molecular weight, carboxy-terminated BAN elastomers. These elastomers were incorporated into rubber-modified epoxy resins which effectively eliminated the T_{ll} transition, except when there was complete phase separation of the rubber and epoxy phases. It was also observed that the intensity of the T_{ll} loss maximum decreased with increasing acrylonitrile content of the copolymer.

There are a few isolated examples of the detection of T_{ll} in random copolymers by DSC;[13,16] these include single examples of an ethylene–vinyl acetate copolymer, a styrene–acrylonitrile copolymer, and a single styrene–ethyl acrylate copolymer. For these last two copolymers the T_{ll} has also been detected by Keinath[27] using DMA.

Experimental Section

Synthesis and Purification. Reagent-grade monomers (styrene and ethyl acrylate) were purified by passage through a column of chromatographic-grade alumina. A solution of monomers (total monomer concentration of 50% (w/w)) in distilled toluene was placed in a polymerization tube; benzoyl peroxide (0.5 wt %) was added, and several freeze–thaw degassings were carried out before the polymerization tube was sealed under vacuum. Polymerizations were carried out in a constant-temperature bath. Upon removal from the constant-temperature bath the ampules were cooled first to room temperature and then to liquid nitrogen temperature and opened. After warming to room temperature, the resultant polymer solution was added to methanol (Waring blender) to precipitate the polymer, which was removed by filtration and purified by two or three additional reprecipitations (from either benzene or toluene) into methanol. Purified copolymer was dried for 48–72 h in a vacuum oven at elevated temperature (50 or 80 °C). (See Table I for details of the samples prepared.)

Characterization. The percent conversion was determined by weighing the purified polymers. The percent composition of the copolymers was determined by NMR spectroscopy in $CDCl_3$ solution at room temperature, using the ratio of the area of the phenyl signal centered at δ 6.98 to that of the CH_2O resonance centered at δ 3.88; the composition was calculated from the average areas of several integration runs. The accuracy of this technique was verified by combustion analysis on two of the copolymer samples; the NMR and combustion analyses gave results within 3% of each other (see Table I).

Because both T_g and T_{ll} are known to be a function of $\bar{M}_n$ and to increase with molecular weight up to a limiting value, we felt it necessary to verify that the prepared copolymers were of sufficiently high molecular weight so that the observed T_g and T_{ll} values would be the asymptotic values, $T_g(\infty)$ and $T_{ll}(\infty)$. Molecular weights for both homopolymers and one of the copolymers were determined by dilute solution viscometry in benzene. The resultant molecular weights varied from 2×10^5 to 3×10^5, and we therefore assume that the molecular weights of all the copolymers were high enough to exhibit limiting values for the two transitions of interest. (The limiting values for PS are reached at ca. 50 000.)

Differential Scanning Calorimetry. DSC thermograms were determined with a Perkin-Elmer DSC-1B and/or a Du Pont

Table I
Characterization Data for Styrene-Ethyl Acrylate Homopolymers and Copolymers[a]

		polymn conditions				
sample	S/EA monomer ratio, %	temp, °C	time, h	convsn, %[d]	composition[b] S/EA, %	mol wt[c] × 10^{-5}
1	0/100	60	12	79	0/100	3.09
2	20/80	60	12	29	38/62[e]	
3	40/60	60	12	20	51/49	2.04
4	50/50	100	48	73	53/47	
5	50/50	80	23	80	55/45	
6	50/50	80	6	44	58/42	
7	60/40	60	12	19	65/35	
8	80/20	60	12	16	83/17[f]	
9	100/0	60	12	15	100/0	2.58

[a] All percentages are weight percent. [b] Determined by NMR analysis (see text). [c] Determined by viscometry in benzene solution. [d] Weight percent yield of purified polymer. [e] 41/59 by combustion analysis. [f] 84/16 by combustion analysis.

910/990. Consistent with the guidelines of Enns,[13,16] the sample size was small (3–15 mg) and the heating rates were relatively fast (usually 40 K/min for the Perkin-Elmer instrument and 10–40 K/min for the Du Pont instrument). The samples were purged with oxygen-free nitrogen. At the end of the initial heating run the temperature was maintained at about 50 K above the expected T_{ll} for 15 min to allow complete flow and fusion; the samples were then normally cooled rapidly, using a liquid nitrogen cooling accessory, before a second heating run. Slower cooling rates did not significantly change the observed results. While we often were unable to detect the T_{ll} transition on second heating runs, Enns[13] consistently observed T_{ll}s on second heating runs of polystyrene if slow cooling and/or annealing at T_{ll}–15 K were employed. For each of the polymers, several different samples were analyzed and multiple runs (2–10) were made on each sample. Temperature was calibrated relative to the melting point of indium for each heating rate used. Base lines were routinely determined and shown to be free of any significant departure from linearity in the temperature region of interest.

Dynamic Mechanical Analysis. Dynamic mechanical testing was carried out with a Du Pont 981 dynamic mechanical analyzer (DMA) in conjunction with a Du Pont 990 or 1090 thermal analyzer programmer/recorder unit and by using the perforated shim stock technique developed by Keinath.[27,29] Samples (20–40 mg) were applied to the shim stock either by solution casting or by melting the sample directly onto the support. The DMA run was initiated at or somewhat below room temperature and a heating rate of 5 K/min was used. The sample was maintained for a few minutes at a temperature about 50 K above the expected T_{ll} before the cooling cycle was started. The cooling cycles normally exhibited considerable thermal lag due to the massive DMA heating block and sample clamp assembly. Temperatures (in the heating mode) were calibrated with the T_g of a poly(methyl methacrylate) standard. Results were displayed as relative damping vs. temperature.

Results and Discussion

The selection of the styrene–ethyl acrylate copolymer system to answer the questions posed in the Introduction was not an arbitrary one; it was selected on the basis of four considerations:

1. High precision refractive index data on the variation of T_g as a function of composition was available for this system from the work of Illers.[32]
2. The large temperature range (>120 K) between the T_gs of the two component polymers (and thus presumably between the T_{ll}s) would result in large changes in the observed transition temperatures as the composition was varied.
3. The expected transition temperatures for this system would be in a temperature range readily accessible by both DSC and DMA.
4. This system is expected to give random copolymers with little tendency toward formation of block or alternating sequences, especially at moderate conversions.

A. DSC Studies. Figure 1 shows representative thermograms for four different S/EA copolymers of varying composition as defined in the caption. The inset to the figure shows a schematic representation of a thermogram for a polymer exhibiting both a T_g and a T_{ll}. The T_g is manifested by an endothermic step jump in the heat flow curve and the T_{ll} is seen as an endothermic slope change in the same curve. The conventions we have utilized to assign both the temperature of the transitions and their intensity (ΔC_p for T_g and Θ for T_{ll}) are also shown.

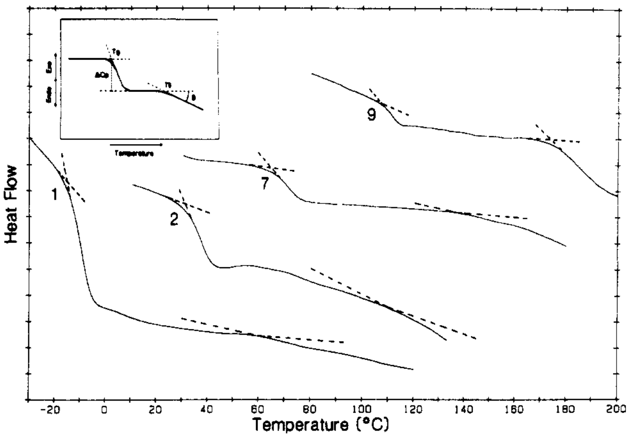

Figure 1. DSC heating traces of four representative samples. The number assigned to each curve corresponds to the sample identification in Table I. Temperatures and intensities of the transitions are discussed in the text. The inset indicates the conventions used for determining both the intensity and position of T_g and T_{ll}. The ordinate axis for thermogram 1 is 1.0 mW/cm while that for the others is 0.5 mW/cm. The traces have been shifted vertically for clarity.

For each of the homopolymers and copolymers, several different samples were analyzed and multiple runs (2–10) were made on each sample. Two different instruments and several different heating rates (see Experimental Section) were used throughout the course of this study.

The thermograms shown in Figure 1 have been shifted vertically for clarity. The number assigned to each curve corresponds to the sample identification shown in Table I. The *Y* axis scaling factor is different for curve 1 (1.0 mW/cm) than for the other three curves (0.5 mW/cm). These four thermograms cover the range of behavior observed in all of the samples.

Curve 1 is a second heating run on an "aged" sample (see below) of poly(ethyl acrylate). This sample exhibited a very intense T_g (ΔC_p = 0.886 J g^{-1} K^{-1}) at −18 °C and a weak T_{ll} transition (Θ = 2.58 rad/100 mg) at 53 °C.

Curve 2 is a first heating run on an as-received (gum) copolymer sample containing 38% styrene; it shows a moderate-intensity T_g (ΔC_p = 0.256 J g^{-1} K^{-1}) at 28 °C and a weak T_{ll} (Θ = 2.37 rad/100 mg) at 107 °C. This sample also shows hysteresis effects (the shallow "well" at the end of the T_g transition), presumably reflecting the prior

Table II
Transitions for Styrene–Ethyl Acrylate Copolymers by DSC and DMA[a]

% styrene[b]	T_g, °C, by DSC[c]	T_{ll}, °C, by DSC[c]	T_{ll}/T_g by DSC	T_g, °C, by DMA[d]	T_{ll}, °C, by DMA[d]	T_{ll}/T_g by DMA
0	−17.2 ± 2.3 (10)	31.5 ± 14.5 (11)	1.19			
38	25.7 ± 1.5 (11)	98.8 ± 11.7 (8)	1.24	42.0 ± 0.0 (2)	105.5 ± 7.8 (2)	1.20
51	42.4 ± 4.5 (11)	104.6 ± 13.8 (7)	1.20	72.0 ± 12.7 (2)	117.5 ± 3.5 (2)	1.13
53	53.3 ± 10.3 (3)	117.0 (1)	1.20	65.0 ± 2.0 (3)		
55	46.0 ± 7.1 (2)	106.0 (1)	1.19	67.0 ± 2.0 (3)		
58	48.3 ± 6.0 (2)	120.0 ± 19.8 (2)	1.22	71.0 ± 2.0 (3)		
65	60.2 ± 1.6 (17)	134.0 ± 4.9 (15)	1.22	80.5 ± 3.5 (2)	164.5 ± 2.1 (2)	1.24
83	74.6 ± 2.0 (4)	138.5 ± 6.4 (4)	1.18			
100	97.5 ± 1.7 (8)	157.6 ± 7.5 (7)	1.16	119.0[e]	170.0[e]	1.13

[a] Error estimates shown are standard deviations of the mean. The number of runs providing data for the mean is shown in parentheses. [b] Expressed as weight percent. [c] Includes data from both first and second heating runs. [d] Data from heating runs only. [e] Data taken from ref 27.

thermal history of the sample. Many of the samples in this study exhibited even larger hysteresis effects upon first heating, which were greatly diminished and/or eliminated in subsequent heating runs with carefully controlled thermal histories.

Curve 7 is a first heating run for a sample containing 65% styrene. It shows a moderate-intensity T_g (ΔC_p = 0.261 J g^{-1} K^{-1}) at 64 °C and a moderately intense T_{ll} (Θ = 4.33 rad/100 mg) at 135 °C. No thermal hysteresis is seen in this sample.

Curve 9 is a first heating run on a powdered PS, of high molecular weight, prepared in this study. This sample, which shows slight thermal hysteresis effects, exhibits a relatively weak T_g (ΔC_p = 0.132 J g^{-1} K^{-1}) at 104 °C and an intense T_{ll} transition (Θ = 20.42 rad/100 mg) at 170 °C.

A summary of the experimental results for the two homopolymers and the seven copolymers studied is presented in Table II. The temperatures reported are the mean values from multiple thermograms; the error estimates (standard deviation of the mean) and the number of runs giving usable data are both shown.

B. DMA Studies. DMA studies were conducted on several of the samples according to the protocol described in the Experimental Section; two different samples were examined for each copolymer studied and both heating and cooling curves were recorded. A representative DMA loss profile for a copolymer containing 38% styrene is shown in Figure 2. In our experimental runs we plot both the resonant frequency (in hertz) and relative damping (in millivolts). The transition temperatures were assigned at the maximum of the loss peak for each transition. The frequencies (at T_g) for the samples examined ranged from 5.0 to 8.4 Hz.

The heating curve shows three characteristic damping peaks at 42, 59, and 100 °C; the cooling curve shows the same three transitions at 3, 36, and 90 °C with an additional shoulder detected on the low-temperature side of the most intense loss peak. The peak at 42 °C (heating run) is assigned as T_g and that at 100 °C as T_{ll}. We believe that the loss peak occurring between T_g and T_{ll} (at 59 °C) is probably an artifact of the perforated shim stock method; it has previously been seen in low molecular weight PS homopolymers and styrene-containing copolymers and its possible origin has been discussed.[27,29,33] These same three loss peaks were evident in all of the DMA samples examined in this study. It should be noted that the shoulder evident on the low-temperature side of the T_g peak in the cooling run shows up in some, but not all, of the samples examined and may be due to the sub-T_g β relaxation. The considerable temperature shift observed between the heating and cooling runs is discussed in the Experimental Section.

A summary of the DMA results is presented in Table II; the numbers given in parentheses have the same meaning as for the DSC results.

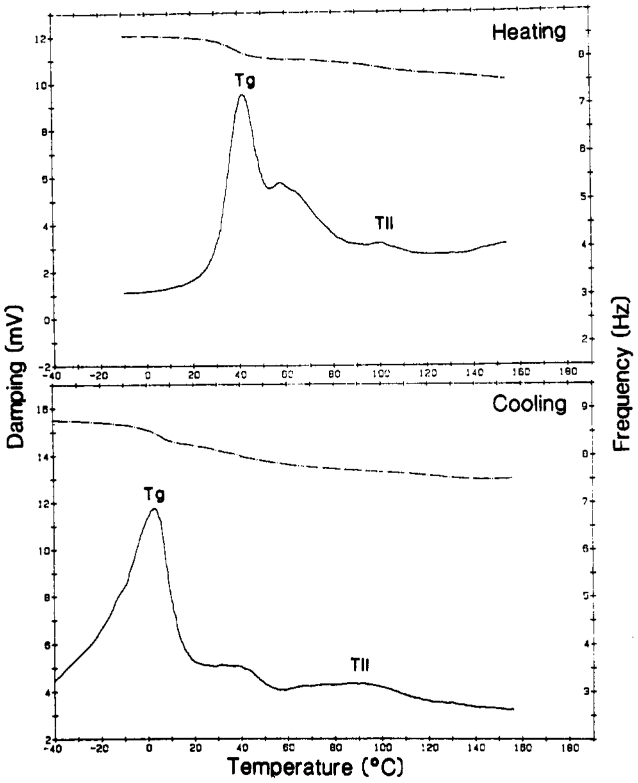

Figure 2. DMA heating and cooling curves for a styrene–ethyl acrylate copolymer containing 38% styrene. The dashed line shows the derivative of the damping curve.

C. Composite DSC and DMA Data. Table II summarizes the mean values and standard deviations for the data collected in this study; the number of experimental runs used in determining these values is also included. The error estimates show consistently less deviation in the DSC data for T_g than for T_{ll}; for the DMA data there seems to be no clear pattern to the deviations, but this data normally represents far fewer experimental runs. The T_{ll}/T_g ratio for the DSC data ranges from 1.16 to 1.24 while the same ratio for the DMA data ranges from 1.13 to 1.24. These tabular data thus answer three of the four questions posed in the Introduction: (1) the T_{ll} relaxation does occur in random copolymers, (2) it can be reliably and reproducibly detected by two significantly different thermal methods—one dynamic (DMA) and one essentially static (DSC), and (3) there is a well-defined relationship (T_{ll} = 1.2T_g) between the two transitions that is not dependent on the experimental method.

The T_gs determined by DSC are approximately 12 °C higher and those determined from DMA heating curves ca. 30 °C higher than the corresponding values determined by Illers for this same system. We believe that this tem-

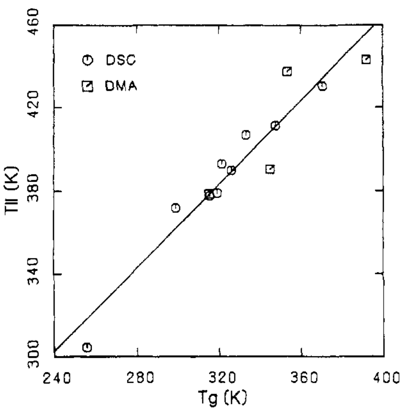

Figure 3. Cross plot (T_{ll} vs. T_g) of composite data from both DSC and DMA on S/EA copolymers. The linear least-squares line fitting the data is shown.

perature shift is due to several factors: thermal lag, the nonequilibrium nature of the DSC and DMA methods, and a shift (especially in the DMA method) due to a frequency effect. We estimate that the frequency for the Illers data is ca. 10^{-2} Hz, that for the DSC measurements is ca. 0.1 Hz (10 K/min), and that for the DMA measurements is ca. 5–10 Hz. For T_{ll} determinations the DMA method results in T_{ll} values that are normally 15–25 °C higher than the corresponding values determined by DSC, presumably for the same reasons indicated above.

The internal consistency of the data gathered in the present study and additional supporting evidence for the constancy of the T_{ll}–T_g relationship are evidenced in the cross plot shown in Figure 3. This representation, which includes all of the data collected from these two methods, has been subjected to computerized statistical regression analysis,[34] leading to the regression line shown. The high correlation ($r = 0.953$) is gratifying, especially considering the diversity of the two methods used. The residuals pattern exhibited by this data set also shows that a linear fit of the data is statistically valid. It should be noted that the regression line does not pass through the origin. We are beginning to accumulate considerable evidence that the T_{ll}/T_g ratio is higher for low-T_g polymers than it is for high-T_g polymers.[5,35] For the regression line in Figure 3 this ratio varies from 1.23 at $T_g = 273$ K to 1.17 at $T_g = 373$ K.

D. Aging Effects On T_{ll}. First heating runs usually give more intense T_{ll} transitions by DSC. If the sample is heated above its T_{ll} on the first DSC run and maintained at a temperature above T_{ll} for some period of time (this is the typical procedure followed in the work reported here), the magnitude of the endothermic slope change at T_{ll} in subsequent heating runs is normally dramatically reduced; it is often virtually impossible to "see" T_{ll} on these subsequent heating runs. During the course of this work we had the occasion to acquire some unique data on the effects of aging on the T_{ll} transition.

The actual sealed sample pans from some of our very early (1979) studies attempting to detect T_{ll} in this copolymer system by DSC were saved. Each of these samples had been subjected to the thermal history described above (i.e., maintained far enough above T_{ll} for sufficient time to allow complete fusion and flow to occur). These samples were then normally allowed to cool to room temperature in the DSC cell before a second heating run was made. At the end of the second heating run the samples were removed from the DSC cell at elevated temperature and placed in storage vials.

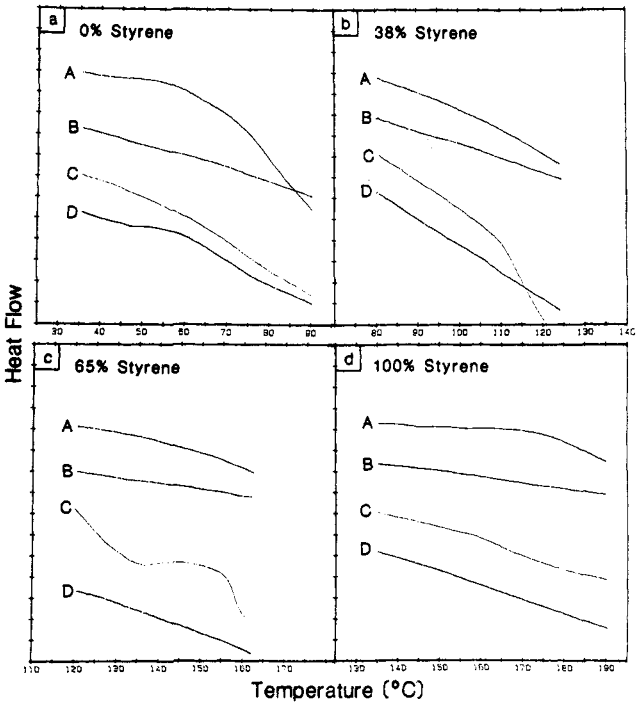

Figure 4. Partial thermograms spanning the expected T_{ll} regions for the two homopolymers and two of the copolymers. The designations A–D refer to specific thermal histories; see text for details. The traces within each quadrant (a–d) of the figure have been shifted vertically for clarity.

As part of the current work we have reexamined, using modern DSC instrumentation, some of these "aged" samples and compared the thermograms with those of "fresh" samples of the identical material studied in the early work. Some pertinent results from this study are shown in Figure 4.

In each part (a–d) of this figure, the four partial thermograms shown (spanning the expected T_{ll} region by at least ±20 K) are displayed on the same temperature axis and recorded at the same Y axis sensitivity although the curves are vertically displaced for clarity. The codes A–D have the same meaning in each part of this figure and represent the following thermal histories: (A) the first heating run on the as-received sample (an elastomeric gum for the ethyl acrylate homopolymer and the two copolymers, a powdered sample for PS homopolymer), placed in an open aluminum sample pan and maintained at elevated temperature (ca. $T_{ll} + 50$ K) before rapid cooling (liquid nitrogen cooling accessory) in the DSC cell; (B) a second heating run on sample A; (C) a current "first" heating run on the as-received sample, sealed in an aluminum sample pan 7 years ago, subjected at that time to the DSC experimentation described above, including being maintained at an elevated temperature and storage since that time in the DSC pan in a sealed vial at ambient conditions; (D) second heating run on the sample from C, recorded within 15 min of sample cooling; at the end of run C the sample was maintained at elevated temperature (ca. $T_{ll} + 50$ K) for 15 min before being cooled as rapidly as possible (liquid nitrogen cooling accessory) while still in the DSC cell.

The 16 partial thermograms shown in Figure 4 display a consistent picture. T_{ll} is clearly evident in first heating runs of as-received material but is absent and/or dramatically reduced in intensity upon a second heating; upon long storage, T_{ll} "grows back in" and can be clearly detected in "first" heating runs on these "aged" samples but then cannot be detected in "second" heating runs performed shortly after this more recent "first" heating run.

To our knowledge, this set of experiments is the first demonstration of the reappearance and/or intensification of T_{ll} transitions as a function of "aging" time. We suggest, however, that this phenomenon is quite consistent with the existence of a loose network in the molten state of polymers between T_g and T_{ll}, with the network held together by segment–segment contacts as first proposed by Frenkel.[6,7] As the sample traverses T_{ll}, "segmental melting" occurs and the melt behaves as a true liquid. One would intuitively expect that these segment–segment contacts would re-form upon cooling of the sample and that T_{ll} would be clearly evident in subsequent DSC runs. The absent, or dramatically less intense, T_{ll} upon second DSC heatings has perplexed us for some time. The "aging" results reported here suggest that at least part of our failure was due to kinetic reasons. The intensity of the T_{ll} transition on a "first" heating of the "aged" samples (thermograms C in Figure 4) are, in some cases, even more intense than those seen in first heatings of as-received samples (thermograms A in Figure 4). We suspect that the rate vs. temperature profile for the formation of segment–segment contacts may show the same type of temperature dependence as that for the crystallization of semicrystalline polymers, i.e., exhibiting a maximum over a narrow temperature range. Thus the rate of re-formation of the necessary "structure" to observe T_{ll} is expected to be a function of both the rate of cooling through the temperature regime where re-formation is rapid and the temperature at which the sample is stored after being heated above T_{ll}.

The extended storage times of the aged samples obviously facilitated our detection of T_{ll} upon subsequent reheating, but it is unclear whether such a long storage time is necessary. A controlled experiment studying the "aging" phenomenon is planned for the near future. It does seem clear that the DSC procedure we have been following is not optimal for the detection of T_{ll} during second heating runs performed shortly after the initial heating runs.

Detection of T_{ll} in these "aged" samples provides additional supporting evidence for the validity of the Frenkel model and clarifies some of our thinking about the thermal reversibility of the events occurring at T_{ll}. We believe that events occurring at T_{ll} are related to a number of diverse phenomena occurring in polymeric systems, including complex rheological behavior in polymeric melts, thermoreversible gelation, and phase homogenization in block copolymers. The first two phenomena have been discussed in a recent review.[5]

Summary and Conclusions

A series of styrene–ethyl acrylate copolymers has been synthesized as a model system for studying the T_{ll} transition in random copolymers. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) studies have been carried out on the copolymers and the two component homopolymers. On the basis of these studies, the following conclusions were drawn.

1. The T_{ll} relaxation does occur in random copolymers.
2. It can be reliably and reproducibly detected by two rather diverse methods (DSC and DMA).
3. The temperature of the T_g transition varies linearly as a function of copolymer composition.
4. The temperature of the T_{ll} transition also varies linearly as a function of copolymer composition.
5. There is a well-defined relationship, $T_{ll} = 1.2T_g$, between T_{ll} and T_g (in degrees kelvin).
6. DSC data on samples aged from 7 years show that the T_{ll} transition, which normally disappears (or is dramatically reduced in intensity) after the sample is heated above T_{ll} for the first time, reappears after long storage at ambient conditions.
7. All of the observed data are consistent with the Lobanov–Frenkel hypothesis for the nature of the molecular events occurring at T_{ll}.

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References and Notes

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