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Heat Capacity Measurements on Polymers and Copolymers of Itaconic Acid Esters Exhibiting Two Glass Transitions

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ABSTRACT: Differential scanning calorimetry has been used to establish the heat capacity (C_p) as a function of temperature for a series of itaconic acid based random copolymers in which the content of *n*-heptyl, *n*-octyl, and *n*-nonyl ester side chains varies from 0 to 100%. Two separate inflections in the C_p–T behavior are observed when the concentration of the long side chain comonomer is ca. 30 mol % and greater. The two processes are also observed as separate relaxations in the dynamic mechanical spectra of the copolymers. The higher temperature inflection is associated with the conventional glass–rubber transition (T_g^u). The temperature of the lower, subambient, inflection (T_g^L) is essentially independent of copolymer composition, and its magnitude (ΔC_p^L) is a function of the concentration of *n*-alkyl side chains in the copolymer. T_g^L is assigned to a separate relaxation process of the *n*-alkyl side chains.

In our previous work on comb-branched polymers it was reported that poly(di-*n*-alkyl itaconates) with side-chain lengths from 7 to 11 carbons exhibit two glass transitions.[1,2] These were observed in both dynamic mechanical measurements and differential scanning calorimetry (DSC). In the former technique, the two glass transitions, designated T_g^u and T_g^L (where u refers to the higher temperature), are evidenced by two major damping peaks, whereas in the latter technique, two distinct inflections in the DSC thermograms are seen. T_g^L has been ascribed to independent micro-Brownian motion of the side chains occurring below the conventional main-chain relaxation T_g^u.

The DSC traces already published[1,2] were nonabsolute in the sense that only exothermic or endothermic changes in the traces were noted. Considerably more information on polymer systems may be obtained by establishing the quantitative heat capacity–temperature (C_p–T) behavior. In a recent study of poly(dicyclooctyl itaconate)[3] the C_p–T curve was shown to contain a contribution from conformational changes of the cyclooctane ring which could be calculated from the known conformational energies of the ring. It was decided that a reinvestigation to obtain absolute C_p–T data for the di-*n*-alkyl itaconate polymers was justified in order to study further the nature of T_g^L and to obtain additional information on the nature of the molecular motion occurring at this transition.

Experimental Section

Sample Preparation and Characterization. Di-*n*-alkyl itaconates with methyl, propyl, heptyl, octyl, nonyl, and decyl side chains were prepared by acid-catalyzed esterification of itaconic acid using the appropriate alcohol, and the pure diesters were isolated by vacuum distillation. Homopolymerization and random copolymerization of the diesters were carried out at 333 K in bulk under nitrogen using α,α'-azobis(isobutyronitrile) (0.5 mol %) as initiator. Polymers were isolated from their chloroform solutions by using methanol as precipitant, and number-average molecular weights ($\bar{M}_n$) were determined at 319 K by membrane osmometry, using either xylene, toluene, or chlorobenzene solutions. Copolymer compositions were estimated by NMR analysis, and all samples were vacuum-dried before use. Composition and $\bar{M}_n$ values are collected in Tables I–IV.

Heat Capacity Measurements. C_p for the homo- and copolymers was measured with a Perkin-Elmer DSC-2 fitted with a low-temperature facility. All measurements were made at a scan rate of 20 K min^{-1} over the temperature range 90–470 K with helium as purge gas. Temperature calibration was monitored with pure metal samples of mercury, gallium, indium, and lead at frequent intervals throughout the series of measurements.

Values of C_p were determined at 5 and 10 K intervals by comparing the recorded output for a polymer sample (~25 mg) with that for a sapphire standard. Both were measured relative to the base line established for empty pans of the same weight as those used for sample and standard. Polymer, sapphire, and base line scans were run consecutively while the liquid nitrogen coolant was maintained at a constant level in the cooling chamber to minimize drift. All measurements were made on polymer samples after quenching from 470 K at a rate of 320 K min^{-1}, although variations in the thermal history of the samples did not appear to alter C_p significantly in the low-temperature region of interest. Detailed numerical data for the C_p-behavior for all systems are available on request from the authors.

Dynamic Mechanical Measurements. The mechanical damping behavior of the homo- and copolymers was measured by using torsion braid analysis (TBA) in which the nominal frequency is 1 Hz. The method has been fully described in previous publications.[2,4]

Results and Discussion

The results of the TBA measurements on the copolymer series poly(di-*n*-propyl itaconate-*co*-di-*n*-octyl itaconate) and poly(dimethyl itaconate-*co*-di-*n*-nonyl itaconate) are summarized in Figures 1 and 2, respectively, as plots of mechanical damping index vs. temperature. These show the same general features as the damping thermograms of copolymers from dimethyl itaconate with comonomers di-*n*-heptyl and di-*n*-octyl itaconate, which have been published previously.[1,2] The copolymer T_g's can be identified throughout the two series by the large damping maximum appearing at the highest temperature, relating eventually to T_g^u of poly(di-*n*-octyl itaconate) at 242 K and to T_g^u of poly(di-*n*-nonyl itaconate) at approximately 275 K. The T_g^u of the latter is rather broad but is in close accord with the value of T_g^u already published[2] for a different sample of this polymer.

T_g^L is not present in copolymers with high dimethyl or dipropyl itaconate contents but is observable as a growing damping maximum, whose position is essentially composition independent, and is located just above 200 K in copolymers with approximately 50 mol % or higher dioctyl or dinonyl itaconate content. The relative intensity of T_g^L increases with increasing concentration of the longer side chain comonomer and is clearly associated with a relaxation process in the octyl and nonyl side chains. The change of comonomer from dimethyl[2] to dipropyl itaconate with dioctyl itaconate does not alter the appearance of the copolymer T_g^L arising from the octyl side chains, which is to be expected if the molecular relaxation process is restricted to the longer side chain.

A third significant damping feature is also present in the TBA thermograms, shown in Figures 1 and 2, at approximately 100 K. This is labeled T_γ and is found in all polymers that contain methylene sequences of at least four carbon atoms (or the sequence –C–C–C–O–). The molecular origins of this low-temperature relaxation have been

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Table I
Copolymer Composition, $\overline{M}_n$ Values, and Details of Transitions Determined by DSC for the Poly(dimethyl itaconate-*co*-di-*n*-heptyl itaconate) Series

sample code	diheptyl itaconate, mol %	$\overline{M}_n \times 10^{-4}$	$T_g{}^u$, K	$T_g{}^L$, K	$\Delta C_p{}^u$, J K^{-1} g^{-1}	$\Delta C_p{}^L$, J K^{-1} g^{-1}
PDMI	0	7.1	377		0.35_2	
P(DMI + DHpI)86/14	14	10.6	312		0.28_4	
P(DMI + DHpI)65/35	35	13.1	290	176	0.23	0.03_4
P(DMI + DHpI)44/56	56	7.7	274	185	0.13_6	0.08_2
P(DMI + DHpI)33/67	67	9.9	260	180	0.07_7	0.08_5
P(DMI + DHpI)23/77	77	10.3	250	183	0.08_9	0.13_0
P(DMI + DHpI)10/90	90	9.7	246	176	0.05_9	0.22_1
PDHpI	100	9.7	248	172	0.04_3	0.14_4

Table II
Copolymer Compositions, $\overline{M}_n$ Values, and Temperatures of Transitions Determined by TBA[2] and DSC for the Poly(dimethyl itaconate-*co*-di-*n*-octyl itaconate) Series

sample code	dioctyl itaconate, mol %	$\overline{M}_n \times 10^{-4}$	TBA			DSC		$\Delta C_p{}^u$, J K^{-1} g^{-1}	$\Delta C_p{}^L$, J K^{-1} g^{-1}
			$T_g{}^u$, K	$T_g{}^L$, K	T_γ, K	$T_g{}^u$, K	$T_g{}^L$, K		
P(DMI + DOI)92/8	8	12.0	359			350		0.33_8	
P(DMI + DOI)78/22	22	15.4	325	213	98	313		0.27_0	
P(DMI + DOI)64/36	36	14.7	305	218	102	290	185	0.21_6	0.02_0
P(DMI + DOI)44/56	56	14.8	278	215	103	269	188	0.13_0	0.04_6
P(DMI + DOI)22/78	78	12.2	257	209	104	252	178	0.06_8	0.15_2
P(DMI + DOI)7/93	93	12.5	243	207	104	242	175	0.05_5	0.23_7
PDOI	100	11.7	242	209	106	240	178	0.04_9	0.28_5

Table III
Copolymer Compositions, $\overline{M}_n$ Values, and Temperatures of Transitions Determined by TBA and DSC for the Poly(di-*n*-propyl itaconate-*co*-di-*n*-octyl itaconate) Series

sample code	dioctyl itaconate, mol %	$\overline{M}_n \times 10^{-4}$	TBA			DSC		$\Delta C_p{}^u$, J K^{-1} g^{-1}	$\Delta C_p{}^L$, J K^{-1} g^{-1}
			$T_g{}^u$, K	$T_g{}^L$, K	T_γ, K	$T_g{}^u$, K	$T_g{}^L$, K		
PDPr	0	8.3	315		98	304		0.25_0	
P(DPrI + DOI)92/8	8	13.5	302		102	284		0.27_4	
P(DPrI + DOI)79/21	21	16.9	280		104	264		0.20_9	
P(DPrI + DOI)60/40	40	8.0	269	201	103	257	188	0.18_1	0.06_7
P(DPrI + DOI)42/58	58	7.8	259	203	105	253	186	0.11_3	0.10_3
P(DPrI + DOI)28/72	72	9.3	253	205	104	248	182	0.06_5	0.17_6
P(DPrI + DOI)18/82	82	12.6	250	207	105	245	180	0.07_0	0.21_3

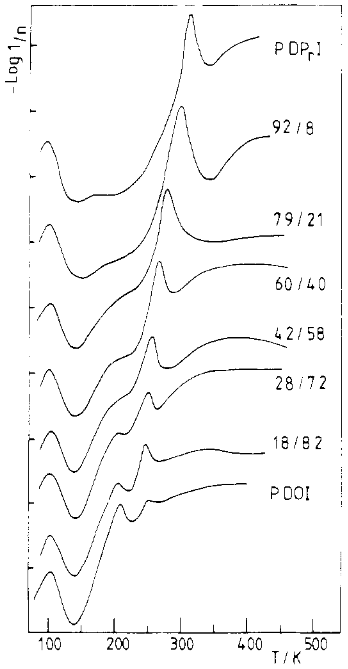

Figure 1. Mechanical damping index vs. temperature for P(DPrI + DOI) series; samples indicated by mole ratio code.

discussed by Cowie.[5] The composition dependences of $T_g{}^u$, $T_g{}^L$, and T_γ, obtained by TBA, for the copolymer series dimethyl[2] and dipropyl itaconate with dioctyl itaconate, and dimethyl itaconate with dinonyl itaconate are shown in Tables II–IV. In the case of $T_g{}^L$ (and T_γ) it can be seen that the temperature of this transition is not strictly composition independent and, although the variations are

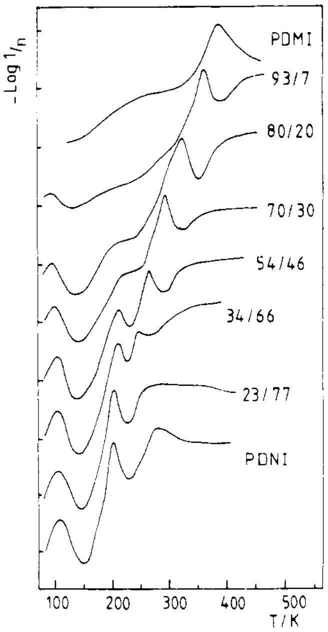

Figure 2. Mechanical damping index vs. temperature for P(DMI + DNI) series.

Table IV
Copolymer Compositions, $\overline{M}_n$ Values, and Temperatures of Transitions Determined by TBA and DSC for the Poly(dimethyl itaconate-*co*-di-*n*-nonyl itaconate) Series

sample code	dinonyl itaconate, mol %	$\overline{M}_n \times 10^{-4}$	TBA			DSC		ΔC_p^u, J K^{-1} g^{-1}	ΔC_p^L, J K^{-1} g^{-1}
			T_g^u, K	T_g^L, K	T_γ, K	T_g^u, K	T_g^L, K		
P(DMI + DNI)93/7	7	12.2	358		98	341		0.33_0	
P(DMI + DNI)80/20	20	12.5	321	218	99	306	180	0.21_2	0.03_0
P(DMI + DNI)70/30	30	13.5	295	223	103	296	195	0.10_4	0.07_6
P(DMI + DNI)54/46	46	14.8	267	213	107	264	184	0.09_3	0.15_7
P(DMI + DNI)34/66	66	14.5	243	211	108	238	188	0.03_8	0.31_4
P(DMI + DNI)23/77	77	13.5		205	108	231	185	0.03_5	0.50_0
PDNI	100	12.2	275	204	108	245	187	0.03_4	0.48_7

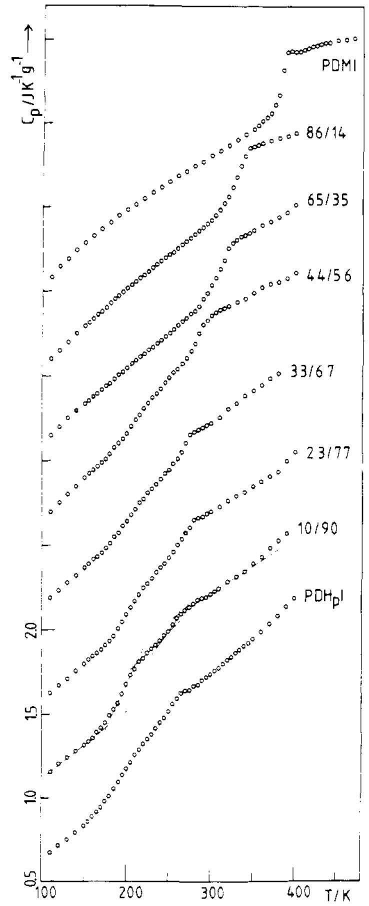

Figure 3. Heat capacity vs. temperature for P(DMI + DHpI) series.

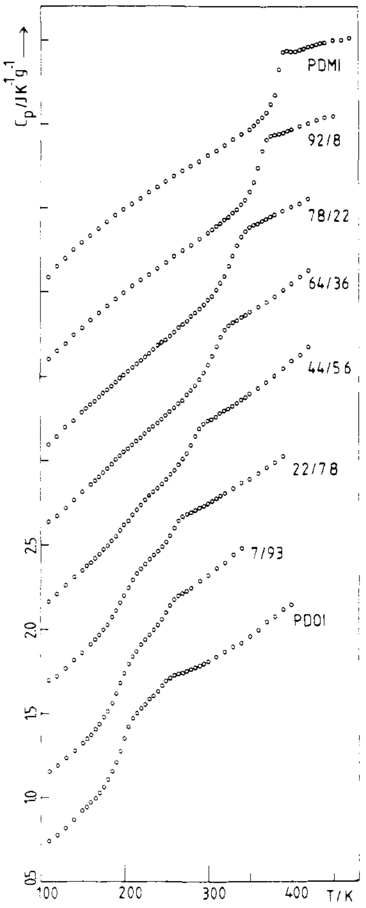

Figure 4. Heat capacity vs. temperature for P(DMI + DOI) series.

small, they may reflect the effect of differences in packing and free volume as the copolymer structure is altered. Change of comonomer from dimethyl to dipropyl itaconate also appears to have an effect, albeit minor, on the relaxation of the longer (octyl) side chains.

The C_p–T behavior of four series of random copolymers prepared from dimethyl itaconate with diheptyl, dioctyl, and dinonyl itaconates and of dipropyl with dioctyl itaconate is shown in Figures 3–6. It is immediately apparent that a relatively smooth monotonic change in C_p, followed by a single sharp inflection defining a glass–rubber transition (T_g), is only obtained for copolymers in which the dimethyl (or dipropyl) itaconate content is greater than approximately 60–70 mol %. For all the other copolymer samples more complex behavior is displayed in the subambient region, and the curves can be interpreted as containing two separate inflections characteristic of a glass transition. This is very clearly seen for copolymers where the concentration of the shorter side chain comonomer is in the 20–30 mol % region.

The position of the lower of the two transitions is again approximately composition independent but the inflection diminishes in intensity as the concentration of the longer side chain comonomer decreases. This lower temperature transition is assigned T_g^L. The position and intensity of the higher temperature inflection are both composition dependent, increasing in temperature and magnitude as the content of the copolymer becomes richer in the shorter side chain component, and this transition is assigned T_g^u. The values of T_g^u and T_g^L are defined by extrapolated onsets of the respective inflections as shown on one of the traces of Figure 3. The extent of the change in C_p at T_g^u and T_g^L (ΔC_p^u and ΔC_p^L) has been estimated from the vertical separation of the lines defining the "base lines" before and after the respective transitions at a temperature half way through the transition. It is recognized that the choice of base line between T_g^L and T_g^u is somewhat subjective in several cases. The values of T_g^u, T_g^L, ΔC_p^u, and ΔC_p^L for all the copolymer series are collected in Tables I–IV.

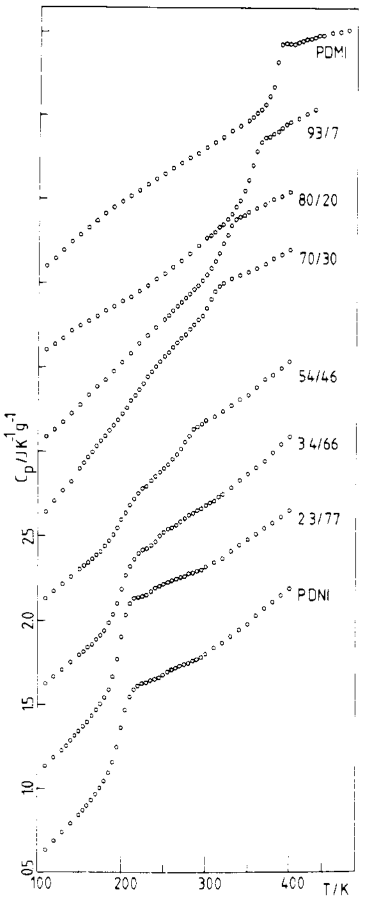

Figure 5. Heat capacity vs. temperature for P(DMI + DNI) series.

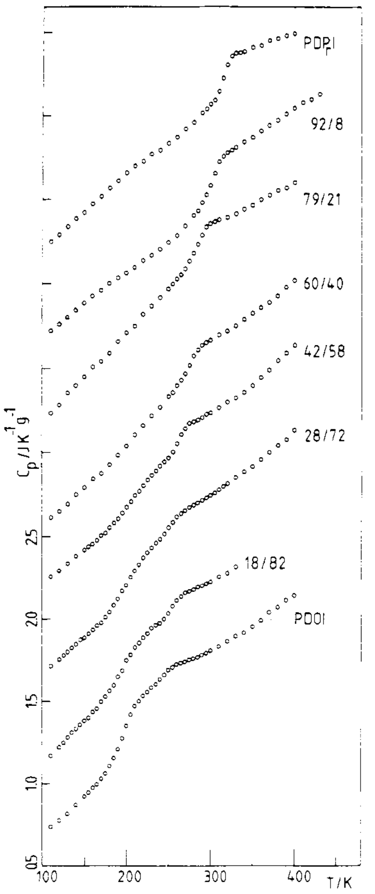

Figure 6. Heat capacity vs. temperature for P(DPrI + DOI) series.

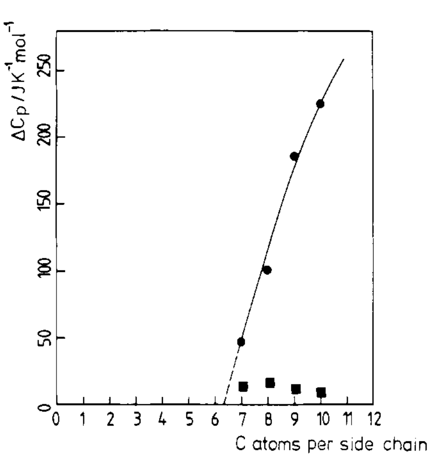

Figure 7. ΔC_p plotted as a function of the number of C atoms per side chain for homopolymer series PDHpI to PDDI: (●) $\Delta C_p{}^{\mathrm{L}}$; (■) $\Delta C_p{}^{\mathrm{u}}$.

The difference between the values of T_g measured by TBA and DSC may be a consequence of two factors. There will be a small difference due to a frequency effect and there may also be some discrepancy introduced because we have chosen the onset temperature rather than the midpoint of the C_p change. The reason for our selection is due partly to the variation in breadths of the transitions as reflected in the C_p changes and it was felt that the onset temperatures would be more consistent for internal comparison.

The series of homopolymers diheptyl to dinonyl itaconate all show substantial changes in heat capacity at $T_g{}^{\mathrm{L}}$, and this might suggest that $T_g{}^{\mathrm{L}}$ is the major change since $\Delta C_p{}^{\mathrm{L}} > \Delta C_p{}^{\mathrm{u}}$. However, this is not the temperature at which the polymer softens. Separate experiments[6] using a Perkin-Elmer thermomechanical analyzer in its penetrometer mode have shown that this occurs at $T_g{}^{\mathrm{u}}$. The C_p–T behavior of poly(di-*n*-decyl itaconate) has also been measured. This is dominated by one major inflection, assigned to $T_g{}^{\mathrm{L}}$ (191 K), and a very much smaller one at ~262 K, assigned to $T_g{}^{\mathrm{u}}$.

$\Delta C_p{}^{\mathrm{L}}$, recalculated in J K^{-1} (mol of repeat units)$^{-1}$ for the homopolymers diheptyl to didecyl itaconate is plotted against side-chain length in Figure 7, where it can be seen that one obtains a smoothly increasing function—further evidence that $T_g{}^{\mathrm{L}}$ is exclusively a relaxation of the *n*-alkyl side chains. It is interesting to note that an extrapolation of the data predicts $\Delta C_p{}^{\mathrm{L}}$ will be zero for a side chain of six or less carbon atoms. This is verified experimentally since no inflection in the DSC curve for poly(di-*n*-hexyl itaconate) can be detected below T_g for this polymer.[7]

Values of $\Delta C_p{}^{\mathrm{L}}$ were not sought for polymers with side chains of more than ten carbon atoms since it is known that side-chain crystallization occurs[2] and the systems are no longer amorphous. An upper limit to $\Delta C_p{}^{\mathrm{L}}$ would be ΔC_p per mole of CH_2 units at the hypothetical glass transition of amorphous polyethylene. This can be estimated from published data[8] to be ca. 15.4 J K^{-1} mol^{-1}, which is sensibly higher than the $\Delta C_p{}^{\mathrm{L}}$ values (per mole of CH_2 units) obtained here. $\Delta C_p{}^{\mathrm{u}}$ for the heptyl to decyl series shows no dramatic or identifiable changes with side-chain length, as would be expected if $T_g{}^{\mathrm{u}}$ represented the onset of main-chain motion only.

The appearance of two separate relaxations for the same polymer implies that there is little or no mixing on the molecular scale between the main and side chains. Molecular models of itaconate polymers confirm this. The main chain of a poly(di-*n*-alkyl itaconate) is almost completely shielded by the pendant ester linkages, which

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provide a polar "barrier" to the approach of an alkyl side chain unit. The polymers are thus visualized as "comb-type" copolymers where the side chains are packed into the regions of space around the polymer backbone but do not penetrate or entangle with the backbone itself.

The behavior of $\Delta C_p{}^{u}$ and $\Delta C_p{}^{L}$ as functions of copolymer compositions can be gauged from the last two columns of Tables I–IV. A definite trend of increasing $\Delta C_p{}^{u}$ with increasing content of the shorter ester side chain is seen and such behavior is rationalized by the postulate that $T_g{}^{u}$ originates primarily from main-chain relaxations. The relative number of main-chain units or segments is small in copolymers with a high, long-ester side-chain content but increases as the copolymer becomes richer in dimethyl or dipropyl itaconate units.

Tables I–IV also show that the $\Delta C_p{}^{L}$ values tend to decrease as the mole fractions of the longer side chains decrease, as would be expected if the relaxations involved are exclusive to these units. $\Delta C_p{}^{\mathrm{tot}} = \Delta C_p{}^{u} + \Delta C_p{}^{L}$ should reflect the overall complexity of the repeat unit or number of "beads"[8] and would be expected to decrease as the copolymers become richer in the comonomer of simpler structure. This is approximately so, but each copolymer series reaches a more or less constant $\Delta C_p{}^{\mathrm{tot}}$ value at ca. 50% composition rather than at 100%. This behavior would seem rather unexpected, and it can only be suggested that the total amount of relaxation that is possible as the rubbery state is achieved occurs over a wider temperature range than encompassed by the two ΔC_p jumps and remains unquantified by $\Delta C_p{}^{u} + \Delta C_p{}^{L}$ as they are defined here.

Finally, it should be noted that the DSC-determined values of $T_g{}^{u}$ and $T_g{}^{L}$ quoted in this paper and derived from C_p–T curves differ considerably from those quoted earlier.[2] The samples used in this study and those used earlier have sufficiently large $\bar{M}_n$ values to ensure that T_g values have reached their asymptotic limit but will differ presumably to some extent in their distribution. This will account for a small part of the observed differences (which is up to 19 K in $T_g{}^{L}$ for poly(di-*n*-decyl itaconate)) but not all. We have found that considerably different values for the onset of a T_g inflection can be inferred from data on the same polymer when it is displayed on a C_p–T curve, as here, compared with the more common DSC trace, which is nonabsolute. This point is being investigated further, but we are of the opinion that the C_p measurements are the more reliable and the values obtained by this method will be more representative of the samples.

Registry No. Dimethyl itaconate–diheptyl itaconate copolymer, 65553-84-6; dimethyl itaconate–dioctyl itaconate copolymer, 78279-12-6; dipropyl itaconate–dioctyl itaconate copolymer, 85864-39-7; dimethyl itaconate–dinonyl itaconate copolymer, 85803-48-1.

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Theoretical Description of the Heat Capacity Change at the Lower Glass Transition Temperature of Poly(alkyl itaconates) Exhibiting Dual Glass Transition Behavior

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ABSTRACT: The change in the heat capacity ($\Delta C_p{}^{L}$) at the lower glass transition ($T_g{}^{L}$) in poly(di-*n*-alkyl itaconates) with 7–10 carbons in the side chain has been measured. A model for a side-chain relaxation mechanism is proposed that involves hindered rotation about C–C bonds, and the relevant partition function and heat capacity contribution from this motion has been evaluated. The calculated heat capacities have been compared with the experimental values in the region of $T_g{}^{L}$, and good agreement has been found.

Introduction

It has been demonstrated that the low-temperature inflections in the C_p–T curves described in the previous paper[1] and labeled $T_g{}^{L}$ for the homopolymer series poly(di-*n*-heptyl itaconate) to poly(di-*n*-decyl itaconate) originate from independent motions of the side chains. In this paper we attempt a theoretical description of the heat capacity behavior at $T_g{}^{L}$ based on a model of side-chain motion.

In the molten state the heat capacity of a high polymer is due to molecular vibrations and, in addition, conformational changes and internal rotations. When the liquid becomes a glass, large-scale molecular motion ceases and the heat capacity is mainly accounted for by vibrational motion only. Smaller contributions that freeze out at $T < T_g$ come from limited internal rotations and movements of small groups of atoms or from changes between rotational isomers of differing energies. To our knowledge, only in the case of poly(dicyclooctyl itaconate) has it been possible to determine experimentally the heat capacity contribution from one such small-scale sub-T_g motion, and this was ascribed to changes of the cyclooctane ring between its nonequienergetic conformers.[2] In the present case the magnitude of the low-temperature inflection ($\Delta C_p{}^{L}$) is very much larger, both relative to ΔC_p at the main-chain relaxation and in absolute terms, when com-

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