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favor the conformational disorder of the chain, according to the model suggested by Corradini and co-workers.[14]

We believe the above considerations represent a potentially useful line of guidance toward the design of improved rubberlike materials.

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Differential Scanning Calorimetry Analysis of Natural Rubber and Related Polyisoprenes. Measurement of the Glass Transition Temperature

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ABSTRACT: A DSC examination of natural rubber (NR) and four related *cis*- and *trans*-1,4-polyisoprenes is reported. Onset T_g values for *amorphous* samples of NR and a synthetic cis analogue are 206 and 208 K, respectively, whereas, the three trans isomers studied had lower values in the range 202–203 K. (These values correspond to rapidly quenched samples heated at scan rates of 20 K/min.) The presence of crystallinity has only a marginal effect on the T_g onset value ($T_g \sim +1$ K) but leads to a more diffuse and indistinct glass transition. Annealing of NR at temperatures close to the observed glass transition leads to observation of distinct endothermal peaks associated with molecular relaxation processes. An investigation of the optimal procedure for measurement of T_g values at low temperatures reveals that scan-rate corrections do not enhance the precision of the results. A procedure is recommended where the glass transition is examined at a moderate scan rate of 20 K/min. The same scan rate is also used for instrument temperature calibration to minimize thermal lag errors.

Introduction

The glass transition temperature (T_g) is a fundamental polymer characteristic, the magnitude of which has a determining influence on the bulk properties of the material. Consequently the measurement of T_g has attracted much attention over the years, and those of most important macromolecules have been widely studied by numerous techniques. Natural rubber (NR) and its synthetic analogues have proved no exception, and T_g measurements by the techniques of dilatometry,[1-4] interferometry,[5] refractive index,[6] thermomechanics,[7,8] NMR,[9,31,32] adiabatic calorimetry,[10] and DSC[11-15,26-30] have been reported (Table I). Correlation of the various literature results is complicated by the time-dependent nature of the glass transition phenomenon, by differences in the thermal histories and purity of the samples, and by variations in experimental procedures (e.g., temperature calibration) and interpretation of the raw data. Thus for NR measured T_g values, as determined by methods of similar time scale, range from 195 to 211 K, whereas for high molecular weight synthetic and naturally occurring *trans*-1,4-polyisoprenes (TPI) T_g values in the range 200–213 K have been reported. Although some aspects of microstructure have been studied,[14,15] the effect of cis/trans isomerization on T_g has not been unambiguously established especially as apparent differences reported in the literature may be attributed to variations in the morphology of the samples.

In recent years DSC has emerged as a rapid, relatively precise, and increasingly popular technique for the determination of polymer T_g values. However, there is to date little uniformity as to the measurement or reporting of such values particularly with regard to parameters such as thermal pretreatment, temperature calibration, scan rate, and specification of T_g value (onset or midpoint).

In light of the above, the present work had dual objectives: (i) the determination of unequivocal values for the T_g of naturally occurring and synthetic *cis*- and *trans*-1,4-polyisoprene; (ii) the establishment of optimal procedures for the DSC determination of subambient T_g values.

Experimental Section

Materials. Natural rubber (DPNR grade) and gutta-percha were native Malaysian samples provided by courtesy of the Rubber Research Institute of Malaysia. The synthetic *trans*-1,4-polyisoprene (TPI) and balata were kindly supplied by Dunlop Ltd., U.K.

The synthetic *cis*-1,4-polyisoprene (NATSYN 2200) was kindly donated by Goodyear, U.S.A., who indicated an isomeric purity of 97–98%.

The intrinsic viscosity $[\eta]$ of the various samples at 30 °C in toluene were as follows: DPNR (7.3 dL/g); gutta-percha (1.43 dL/g); TPI (3.0 dL/g); balata (1.7 dL/g); natsyn (3.8 dL/g).

DPNR and the natural and synthetic *trans*-polyisoprene showed no detectable steric impurities by ^{13}C NMR.

Purification of the above samples by reprecipitation from toluene and vacuum-drying showed no discernible affect on measured T_g values.

DSC Measurements. All measurements were made with a Perkin-Elmer DSC-2C equipped with a liquid nitrogen subambient cooling accessory and employing helium as purge gas. In order to ensure good reproducibility the liquid nitrogen reservoir was filled 2 h before calibration and maintained approximately

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Table I
Summary of Literature Values of T_g for *cis*- and *trans*-Polyisoprenes

sample[a]	method	T_g, K	comment	ref
NR	dilatometry	203, 201, 200, 201	rate 1 K/min	1-4
NR	interferometry	202-206		5
NR	refractive index	198		6
NR	thermomechanics	200		8
NR	adiabatic calorimetry	195-201		33
NR	DSC	204	cross-linked sample	11
NR		202	rate extrapolated to 0	15
NR		211	rate 20 K/min	26
NR	NMR	223, 246	80, 4 × 10^4 Hz	9, 31
CPI	dynamic mechanics	205	7% 3, 4 units	7
CPI	adiabatic calorimetry	200	97% cis	10
CPI	NMR	223		32
CPI	dilatometry	223		32
CPI	DSC	209	95%, 80% cis	11, 27
C/TPI	DSC	209	rate extrapolated to 0, 40 K/min	13, 14
		205, 211	rate extrapolated to 0, 20 K/min	15
TPI	dynamic mechanics	200		7
TPI	dilatometry	213	balata	1
TPI	DSC	203, 207, 213		30, 12, 29

[a] NR, natural rubber; CPI, synthetic high *cis*-1,4-polyisoprene; C/TPI, synthetic high *cis/trans*-1,4-polyisoprene; TPI, *trans*-1,4-polyisoprene either synthetic or natural. Where more than one T_g value is cited per entry the order of values corresponds to the order of remarks or references.

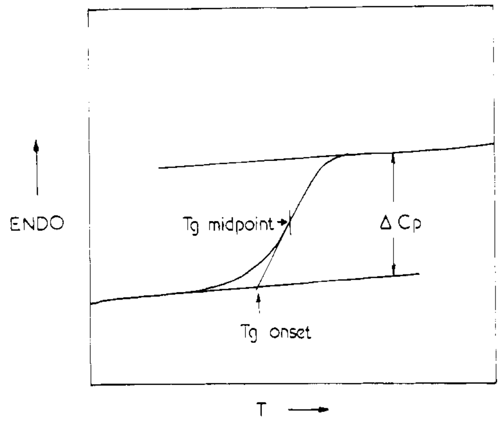

Figure 1. Glass transition—definition of parameters.

three-fourths full throughout measurement. The instrument was calibrated against mercury, water, and indium at 10 K/min and the calibration cross-checked against a set of NBS low-temperature standards (vide infra). For crucial measurements the calibration was checked against a cyclohexane standard before and after examination of the sample.

Polymer samples (ca. 10 mg) were encapsulated in the standard aluminum pans, heated at 400 K for 5 min, and quench cooled (programmed cooling rate 320 K/min) to about 50 K below the anticipated glass transition temperature. Heating scans were run at rates reported in the text. Samples were requenched before heating at a different rate.

Samples such as balata and the synthetic TPI, which undergo rapid crystallization, were also quenched by an alternative method (*external quenching*) whereby the encapsulated sample was heated at 400 K, plunged directly into liquid nitrogen, and inserted into the DSC instrument at 150 K—a temperature well below the glass transition.

Glass transition onset and midpoint values (Figure 1) were determined with the Thermal Analysis Data Station (TADS) standard program supplied by Perkin-Elmer. The overall reproducibility of measurement and calculation was found to be ±0.1 K for samples of NR examined at a scan rate of 20 K/min.

Results and Discussion

Temperature Calibration. Particular attention was paid to the problem of temperature calibration since although the instrument manufacturer claims a linear response over the whole range of interest, it is still necessary to define the absolute position of the scale. The temperature scale was set with respect to the known melting transitions of highly pure mercury (T_{onset} = 234.28 K), water (T_{onset} = 273.15 K), and indium (T_{onset} = 429.78 K) and was subsequently cross-checked with a series of four ICTA-certified organic reference materials, as supplied by the U.S. National Bureau of Standards. The results (Table II) confirm the accuracy of the calibration and the linearity of the temperature scale for this particular instrument. It is noteworthy that despite lower thermal conductivities organic calibrants do not show significant variation in temperature calibration from the metallic counterparts.

Table II
Temperature Calibration

	onset of melting transition, K		
reference	lit.	ICTA[a]	exptl[b]
cyclohexane	186.3	187.1 ± 3.5	186.1 ± 0.2
	279.9	278.0 ± 1.1	279.3 ± 0.2
1,2-dichloroethane	237.5	237.3 ± 2.0	236.3 ± 0.1
diphenyl ether	300.1	298.6 ± 2.2	299.1 ± 0.1
o-terphenyl	329.4	328.2 ± 2.2	328.9 ± 0.2

[a] Mean values of DTA measurements from 14 laboratories. [b] Mean of three determinations (this study).

Table III
Effect of Scan Rate on Observed Transition Temperatures for Cyclohexane

scan rate, K/min	T_{onset},[a] K	T_{max}, K
2.5	186.5	187.6
5	186.3	187.7
10	186.3	188.1
20	186.5	188.7
40	185.9	189.2

[a] Value used for temperature calibration.

The calibration drift of the instrument operated with liquid nitrogen coolant, over a period of 6 h, was monitored by a series of measurements at various intervals and was shown not to exceed ±0.3 K of the initial calibrated value.

Variation of scan rate, which is discussed more fully below, has only a moderate effect on the measured tem-

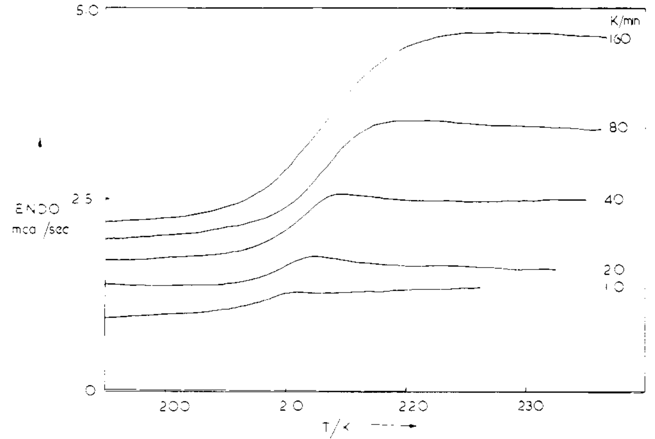

Figure 2. Effect of scan rate on the NR glass transition.

Table IV
Effect of Scan Rate on the Breadth of the Observed Glass Transition for NR

scan rate, K/min	T_g, K onset	T_g, K midpoint	ΔT,[a] K
10	205.0	206.3	1.3
20	206.3	208.2	1.9
40	206.9	209.3	2.4
80	207.5	210.8	3.3
160	206.6	211.8	5.2

[a] $\Delta T = T_{g_{\text{midpoint}}} - T_{g_{\text{onset}}}$.

perature over the range 2.5–40 K/min (Table III), the effect being negligible for the onset measurement.

Dependence of Glass Transition Temperature on Scan Rate. An important variable in DSC measurement of T_g is the programmed heating rate. Increasing the scan rate leads to a concomitant increase in the magnitude of the base-line shift accompanying the transition from the glass to liquid phase and hence improves the detectability of the transition (Figure 2). However, at the same time, the position of the T_g is shifted to higher temperatures, and the divergence of the onset and midpoint values is increased (Table IV).

This variation of apparent T_g with DSC heating rate has generally been attributed to the thermal lag of the sample, which increases in step with the heating rate.[16-18] This thermal lag is considered[17] to comprise a machine path error and a sample error which are dependent on the characteristics of the instrument and sample, respectively. A theoretical analysis[18] of the heat flow has shown that the anticipated temperature shift should be dependent on the square root of the heating rate, heat of fusion, and sample mass. This was confirmed experimentally for the fusion of low molecular weight compounds.[18] Thus, generally, temperature corrections have been applied in polymer analysis by measurement of the transition temperature as a function of scan rate (ν) and extrapolation of T vs. $\nu^{1/2}$ to 0.[14,19] Alternative empirical extrapolations such as T vs. ν,[17] log T vs. ν,[17,27] or T vs. log ν[16] have also been employed.

However, it must not be overlooked that T_g itself is a rate-dependent parameter, and a dependence on scan rate is to be anticipated over and above any thermal lag errors. Thus, on the basis of the hole theory of liquids, Wunderlich et al.[20] have shown that over a restricted range of heating rates (ca. 1–60 K/min) the time-dependent nature of the glass transition may be adequately described by an equation of the form

$$\log \nu = A - B/T_g \qquad (1)$$

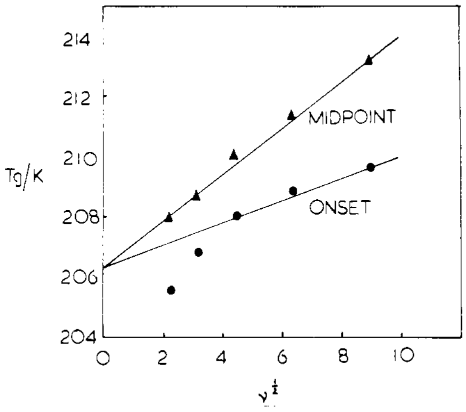

Figure 3. Scan-rate correction for NR T_g measurements: plot of T_g vs. $\nu^{1/2}$.

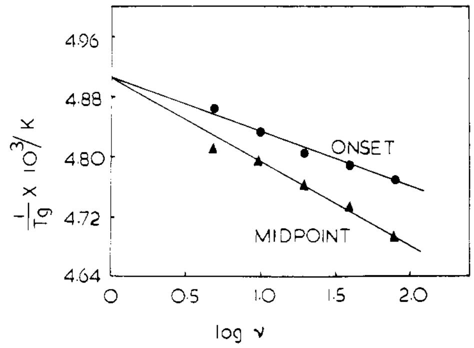

Figure 4. Scan-rate correction for NR T_g measurements: plot of $1/T_g$ vs. log ν.

Thus it appears likely that the observed T_g shift is a composite of the two effects, which may not readily be separated, and consequently the extrapolated value may be of dubious thermodynamic significance. A further complication is the observation[36] that the measured T_g may also be dependent on the thermal pretreatment of the sample. Thus in the case of polystyrene, as the rate of cooling through the glassy region is lowered, T_g has been found to decrease by 2.2 K per decade decrease in cooling rate.[36]

The effect of scan rate on the observed T_g for NR is summarized in Figures 3 and 4, where the data are corrected by both square root and log relationships. As is typical of all the various samples of NR examined the best fit is provided by eq 1, suggesting that the heat flow correction is less important than the kinetic nature of the glass transition. Consistent with this is the observation in these studies that the measured T_g is effectively independent of the sample mass over the range 5–15 mg. It is noteworthy that both extrapolations lead to a coincidence of the midpoint and onset values of the T_g.

However, these extrapolations are much less satisfactory for the *trans*-1,4-polyisoprenes. Thus gutta-percha (GP) consistently gives scattered data points and a positive slope for T_g onset values, whereas balata generally shows an *increase* in T_g on extrapolation (Figure 5). This odd behavior may be a consequence of the tendency of the *trans*-1,4-polyisoprenes to undergo crystallization even at low temperature and on quench cooling (vide infra).

In view of the above results the authors are of the opinion that there is little to be gained by the use of scan-rate corrections in the measurement of polymer glass transition temperatures. The optimum procedure would appear to be to study the glass transition phenomenon at moderate scan rates (e.g., 20 K/min) identical with or close to those employed for instrument calibration. This con-

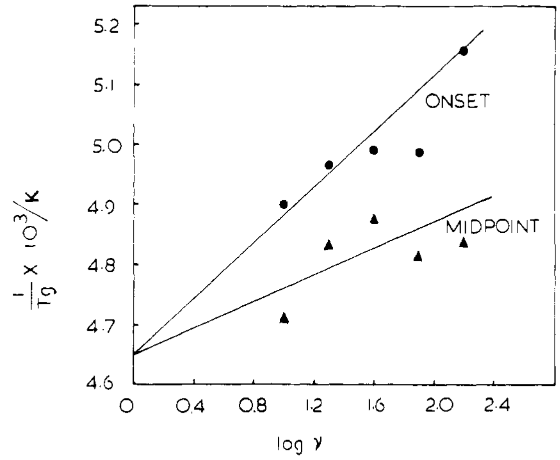

Figure 5. Scan-rate correction for balata: plot of $1/T_g$ vs. log ν.

Table V
Comparison of Extrapolation Procedures[a]

extrapolation	T_g, K
lit.[b]	205.2
T_g vs. $\nu^{1/2}$	202.2
T_g vs. ν	203.3
$1/T_g$ vs. log ν	203.1

[a] Data taken from ref 15, Table I, sample L-11B.
[b] Value quoted in ref 15 for extrapolation to a heating rate of 0 K/min.

clusion is based on the following observations:

(i) Recommended instrument calibration procedures, adhered to by most authors, call for measurement with standard compounds at a single scan rate and hence the thermal lag is not corrected in the calibration step. However, provided that sample and standard are measured at similar scan rates, the errors due to thermal lag are largely compensated.

(ii) The choice of extrapolation procedures as applied to polymer T_g measurements appears somewhat arbitrary. Furthermore, the procedures are of restricted applicability, and different methods lead to distinct extrapolated values. An apposite example is the recently reported[15] evaluation of T_g values for high 1,4-polyisoprene. Data from that publication have been reevaluated and are summarized in Table V. Each extrapolation procedure yields distinct results that are at variance with the quoted value,[15] derived by extrapolating to a heating rate of zero by an unspecified method.

(iii) In our experience, the precision of the extrapolated T_g value is significantly less than that determined from repetitive measurements at 20 K/min. Similar observation have been made earlier.[28] This may in part be due to the inexactness of the relationships used for extrapolation and in part due to the rather poorer reproducibility that is encountered when measuring at very low scan rates. (For NR, the standard deviation of five determinations deteriorates from ±0.1 K at 20 K/min to ±0.4 K at 2.5 K/min.)

(iv) Extrapolation procedures are significantly more time consuming and may be conducted at the expense of careful calibration.

The Influence of Microstructure on T_g. In order to undertake a meaningful comparison of the effect of cis/trans isomerization on T_g, care was taken to ensure that the samples studied were essentially amorphous. Whereas for *cis*-polyisoprenes and GP rapid quenching (320 K/min) from 400 K sufficed, in the case of balata and TPI, samples quenched in this manner were still highly crystalline (Figure 6). However, *external quenching* of these *trans*-polyisoprenes provided samples that were essentially amorphous, as judged by the subsequent crystallization endotherm on heating above T_g (Figure 6).

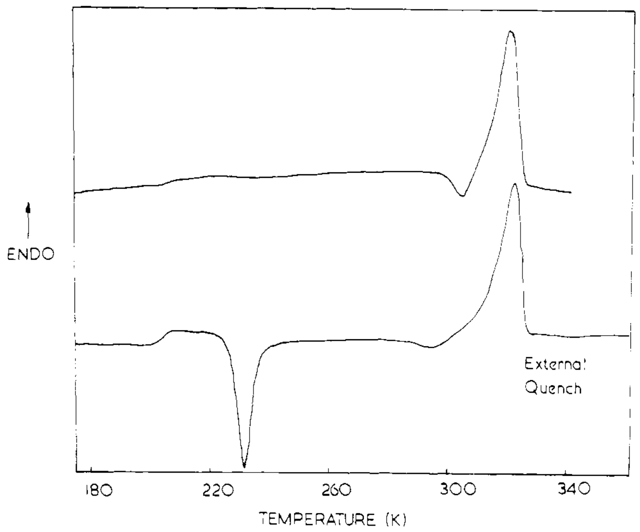

Figure 6. Comparison of the DSC scans of TPI quenched in the instrument and externally.

Table VI
Glass Transition Measurements for Various Amorphous *cis/trans*-Polyisoprenes

sample	T_g,[a] K onset	T_g,[a] K midpoint	ΔC_p, cal g^{-1} K^{-1}
cis			
natural rubber	206.3 ± 0.1	208.2 ± 0.2	0.104 ± 0.007
CPI	207.8 ± 0.2	209.8 ± 0.3	0.110 ± 0.004
trans			
balata	201.8	203.7	0.101
gutta-percha	203.0 ± 0.1	205.0 ± 0.1	0.107 ± 0.003
TPI	201.6	203.4	0.103

[a] Mean of five values except for balata and TPI.

The T_g values summarized in Table VI are derived from measurement and temperature calibration at a scan rate of 20 K/min. At this scan rate the reported midpoint values are consistently 2 K higher than the T_g onset values for all the samples. It can be seen that the T_g of the cis polymers are from 3 to 6 K higher than the trans counterparts, depending on the source of the samples. The NR glass transition is marginally lower than that of the synthetic cis analogue, and this may be due to a trace amount (~1%) of 3,4-isomer in the latter polymer since it has been shown that the presence of this unit markedly increases the T_g of polyisoprene.[14,15]

That GP has a comparatively higher T_g than the other *trans*-polyisoprenes is not readily explicable but is consistent with the greater rotational freedom associated with the latter polymers as evidenced by their facile crystallization.

The observed T_g values are generally in agreement with the earlier literature (Table I) but refute the common observation[21] that the trans isomers exhibit higher glass transitions.

The change in heat capacity (ΔC_p) on passing from the glassy to the rubbery state are essentially identical for all the samples and are close to a value of 0.110 cal g^{-1} K^{-1} deduced from earlier literature results for NR.[34] This again confirms the essentially amorphous structure of the examined samples.

The Influence of Crystallinity on T_g. The effect of crystallinity on polymer T_g measurements has not been unequivocally established, and both increased and de-

Table VII
Glass Transition Measurements for Various Crystalline *cis/trans*-Polyisoprenes

sample	T_g, K onset	T_g, K midpoint	ΔC_p, cal g^{-1} K^{-1}	ΔH_{fus}, cal/g
natural rubber	206.6 ± 0.2	209.3 ± 0.3	0.050 ± 0.003	5.3
balata	202.3 ± 0.3	205.4 ± 0.5	0.023 ± 0.004	10.8
gutta-percha	204.4 ± 0.5	207.9 ± 0.5	0.027 ± 0.005	12.1
TPI	202.8	206.8	0.042	10.8

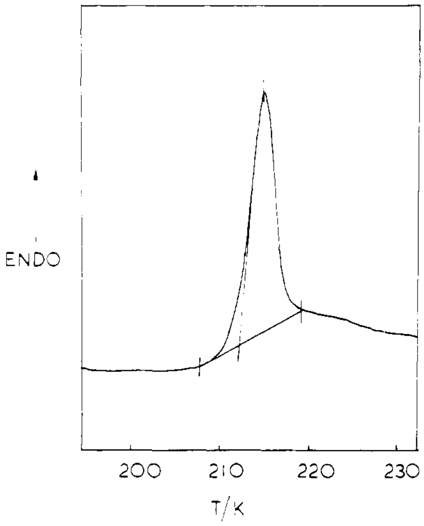

Figure 7. Effect of annealing on the observed glass transition for NR.

creased values of T_g have variously been reported. In this study samples of *trans*-polyisoprenes crystallized at ambient temperatures and NR crystallized at 248 K overnight were employed. The synthetic cis analogue of NR showed no tendency to crystallize when annealed at 248 K overnight, and this may be attributed to trace amounts of steric impurities (vide supra) which inhibit crystallization.

The T_g values for the semicrystalline polymers (Table VII) are seen to be from 0.3 to 1.4 K higher than the comparable amorphous samples, depending on the extent of crystallinity. At the same time the observed glass transition is broader than for the amorphous samples; i.e., the midpoint value is from 3 to 4 K higher than the T_g onset value. This may reflect the superimposition of more than one T_g characteristic of longer or shorter amorphous segments between adjacent crystalline regions. As anticipated the magnitude of the ΔC_p values for the glass transition are markedly reduced, the effect being most pronounced for the samples of highest crystallinity.

It can be concluded that the presence of crystalline regions in polyisoprenes leads to a small elevation of the glass transition temperature by reducing the mobility of the amorphous regions, in a manner analogous to the introduction of chemical cross-links.[11,35]

The Influence of Annealing on the Glass Transition Phenomenon. It has been generally observed that slow cooling[13,22] of polymers through the region of the glass transition or, alternatively, isothermal treatment[23-26] of quench-cooled polymers close to T_g leads to endothermal peaks superimposed on the glass transition.

Such phenomena are shown by both NR and GP annealed at temperatures close to the glass transition (Figure 7). The magnitude of the endotherm increases with annealing time and is dependent on the annealing temperature (Figure 8). The effect is a maximum at annealing temperature very close to or slightly below the glass transition, which is exactly analogous to the results obtained for PVC homopolymers.[24]

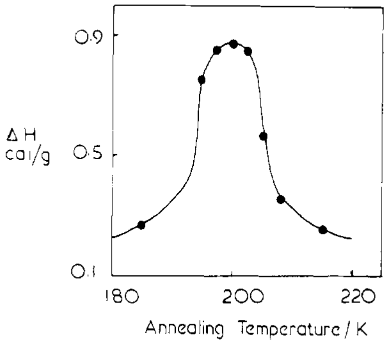

Figure 8. Effect of annealing temperature on the magnitude of the endotherm associated with the NR glass transition.

Qualitatively these effects can best be understood in terms of relaxation processes. Thus the quench cooling of a polymer from the rubbery state allows insufficient time for the macromolecules to reorientate and approach equilibrium conformations. The polymeric sample is thus frozen in a metastable state which is characteristic of a much higher temperature. If the metastable sample is subsequently annealed at temperatures *close* to the glass transition, then reorientation of the polymer sample can slowly occur to approach the equilibrium state characteristic of that temperature. At temperatures much lower than T_g the process is kinetically too slow to be readily observable, while at much higher temperatures the degree of conformational change will be dramatically reduced and the effect diminished.

On subsequent reheating of the polymer sample at moderate rates (e.g., 20 K/min), an endothermal peak is observed some degrees above the annealing temperature as a consequence of the rapid endothermic coiling of the chains, which initially lags behind the heating rate. At higher temperatures, the segmental motion of the chains rapidly increases and the equilibrium polymer conformation is maintained, without further drastic jumps.

For measurement of glass transition temperatures it is preferable to avoid the complication of such annealing affects by rapid quenching of the sample to a temperature some 40–50 K below the anticipated T_g. Such a procedure has been adopted in the present study.

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Positron Annihilation Studies of the Glass-Rubber Transition in Poly(alkyl methacrylates)

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ABSTRACT: Positron annihilation lifetime measurements are reported on poly(methyl methacrylate), poly(ethyl methacrylate), poly(isobutyl methacrylate), and poly(*n*-butyl methacrylate) over a temperature range that includes the glass transition temperature. The long-lifetime component exhibits a similar variation to that observed in similar glass-forming simple liquid systems. The interpretation of the data based on a free-volume model and using ultrasonic data to define a mean cavity size allowed rationalization of the data on all the systems. A close inspection of the variation of the intensity of the long-lifetime component, τ_3, showed evidence for the effects of motions associated with the alkyl side chains on the free-volume in the solid polymer and hence on the probability of formation of orthopositronium.

Introduction

Technologically the glass-rubber transition (T_g) is perhaps one of the most important characteristics of an amorphous polymer. During the last 30 years a number of theories have been put forward to explain this phenomenon and all involve the concept of entropy or free volume as being the controlling feature associated with the T_g process.[1] Studies of the specific heat,[2] modulus of elasticity,[3] coefficient of self-diffusion,[4] and mechanical,[5] dielectric,[6] and ultrasonic[7] relaxation have all been interpreted on the basis of the free-volume model. The free-volume model[8] has been widely applied to the interpretation of the physical properties of glassy polymers. Our previous studies of glass-forming liquids[9-11] have indicated that the positron annihilation technique is capable of probing the temperature variation of the cavity size in which it is formed. The latter appears to be closely related to the free volume, which is used to describe the temperature dependence of the glass transition processes as observed by many relaxation techniques. The position annihilation technique has been used extensively for the investigation of the glass-rubber transition in polymer systems,[12-36] and this topic has been recently reviewed by Stevens.[36] In this paper we attempt to explore the use of positron annihilation for the characterization of the glass-rubber transition in a system in which both backbone and side chain motion is also possible.

Many studies have been reported on positron annihilation in polymers; however, many of these studies use commercial polymers of ill-defined composition, thermal history, or molecular weight. Despite these limitations on the definition of the system, it is clear that the method is capable or providing useful information on the glass state of polymers. The positron on entering the solid will induce ionization of the material through which it passes, generating free electrons and losing energy in the process.[37] Positronium is formed and trapped into a cavity.[38] If the spins of the positron and electron are antiparallel, parapositronium is formed, whereas if they are parallel orthopositronium is formed. The annihilation of parapositronium is quantum mechanically allowed and occurs in 125 ps, whereas annihilation of orthopositronium would take approximately 140 ns in a vacuum.[39] Annihilation of the orthopositronium occurs via pick-off[12] processes, the probability of which is directly related to the inverse of the cavity dimensions and to the electron density of the cavity wall. The lifetime of the orthopositronium is therefore directly related to cavity size,[9] which in turn reflects the free-volume distribution in the polymer solids.

Positron annihilation lifetimes have been measured as a function of temperature,[12,20] pressure,[36], and electric field[2,3,25,30] in nylon, polyethylene, elvicite, polystyrene, poly(vinyl chloride), Teflon, and polyisoprene.[12,20,23-25,30,36] The majority of the samples used were commercial in origin and probably contained plasticizer and antioxidant as well as fillers. There have, however, been a number of studies in which the polymers were better characterized and these reveal the strength of the technique to provide data on the free-volume distribution in the system. Studies by Stevens et al.[20,21] on two well-defined polymers, poly-

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