Ultrasonic relaxation studies of poly(isobutylene) in *m*-xylene

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(Received 9 November 1979; revised 2 February 1980)

Ultrasonic measurements are reported on solutions of two different samples of poly(isobutylene), one relatively regular—CH_2—$C(CH_3)_2$—(Vistanex L80) and one with considerable structural irregularity such as chain branching (Vistanex L140). Measurements were carried out from 303—353K in *m*-xylene over a frequency range 1—100 MHz. A low frequency normal mode (viscoelastic) and a higher frequency conformational absorption are observed. The temperature dependence of the conformational absorption reveals a pseudo helix—coil transition at around 323K. Above this temperature, the two polymers show temperature coefficients of different sign. This phenomenon is explained in terms of a lower energy difference between conformational states in the branched chain polymer.

INTRODUCTION

Although poly(isobutylene) has been used widely as a model for calculation of polymer configurational statistics in solution, the detailed dynamics of conformational change remain obscure. Early ultrasonic observations[1,2] were concerned with very concentrated solutions and bulk polymer, and are little help in elucidating the conformational characteristics of dilute solution. Studies[3–24] of the thermodynamic and viscoelastic properties of dilute solutions have shown how these depend on the nature of the solvent and on the crystallinity of the polymer, but again give no information on the conformational dynamics.

Studies of n.m.r. relaxation in the bulk polymer have been focussed on the strength of interaction between neighbouring methyl and methylene groups[25–36]. It has been proposed that the main contribution to the relaxation arises from amorphous regions which exist between more helical conformations. To support this, studies of the spectral changes on dissolution of the polymer have indicated that short range helical structures can exist in solution at room temperature[25].

In the previous study of polystyrene in toluene and xylene[37], the temperature variation of the ultrasonic absorption was consistent with destruction of helical sequences of the polymer. In view of the fact that poly(isobutylene) also exhibits helical structure in solution, it was thought that similar effects might be detected in this system. Thus, with present knowledge of the various factors contributing to acoustic absorption in dilute solutions, it should be possible to evaluate and explain the detailed behaviour of poly(isobutylene).

EXPERIMENTAL

Materials

Two samples of poly(isobutylene) were studied. These were commercial samples obtained from Esso Chemicals Ltd. and have the trade names Vistanex L80 and L140. Samples with the same code names have been used by other workers for the determination of the thermodynamic properties in solution. G.p.c. determination of the molecular weight indicated that the polymers have $\bar{M}_n$ values of 4.22×10^5 and 6.11×10^5, respectively, both with $\bar{M}_w/\bar{M}_n$ approximately 2.2. ^{1}H-n.m.r. spectra at 220 MHz are shown in *Figure 1*. The ratio of the methylene to methyl protons should be 1:3, if the polymer conforms to the ideal regular structure:

$$-(CH_2-C(CH_3)_2)-_n$$

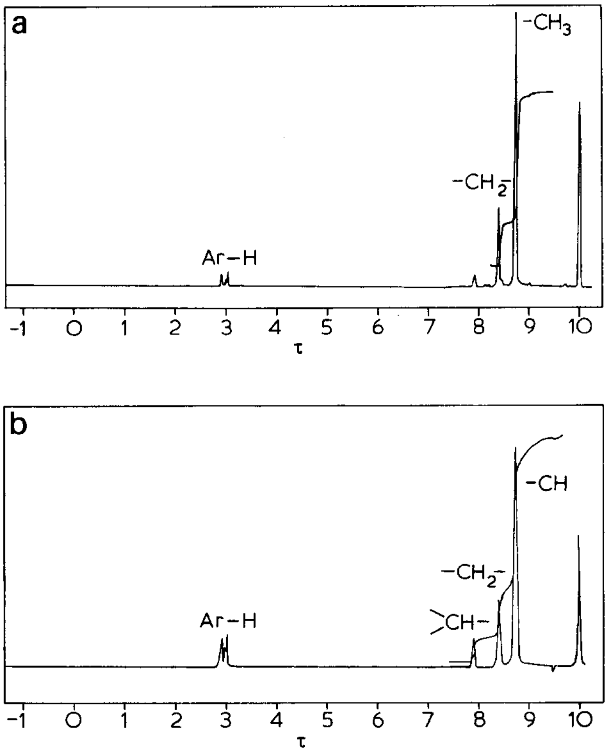

Figure 1 ^{1}H-n.m.r. spectra for poly(isobutylene) samples. Sweep widths 2500 c s^{-1}. a, Vistanex L80; b, Vistanex L140

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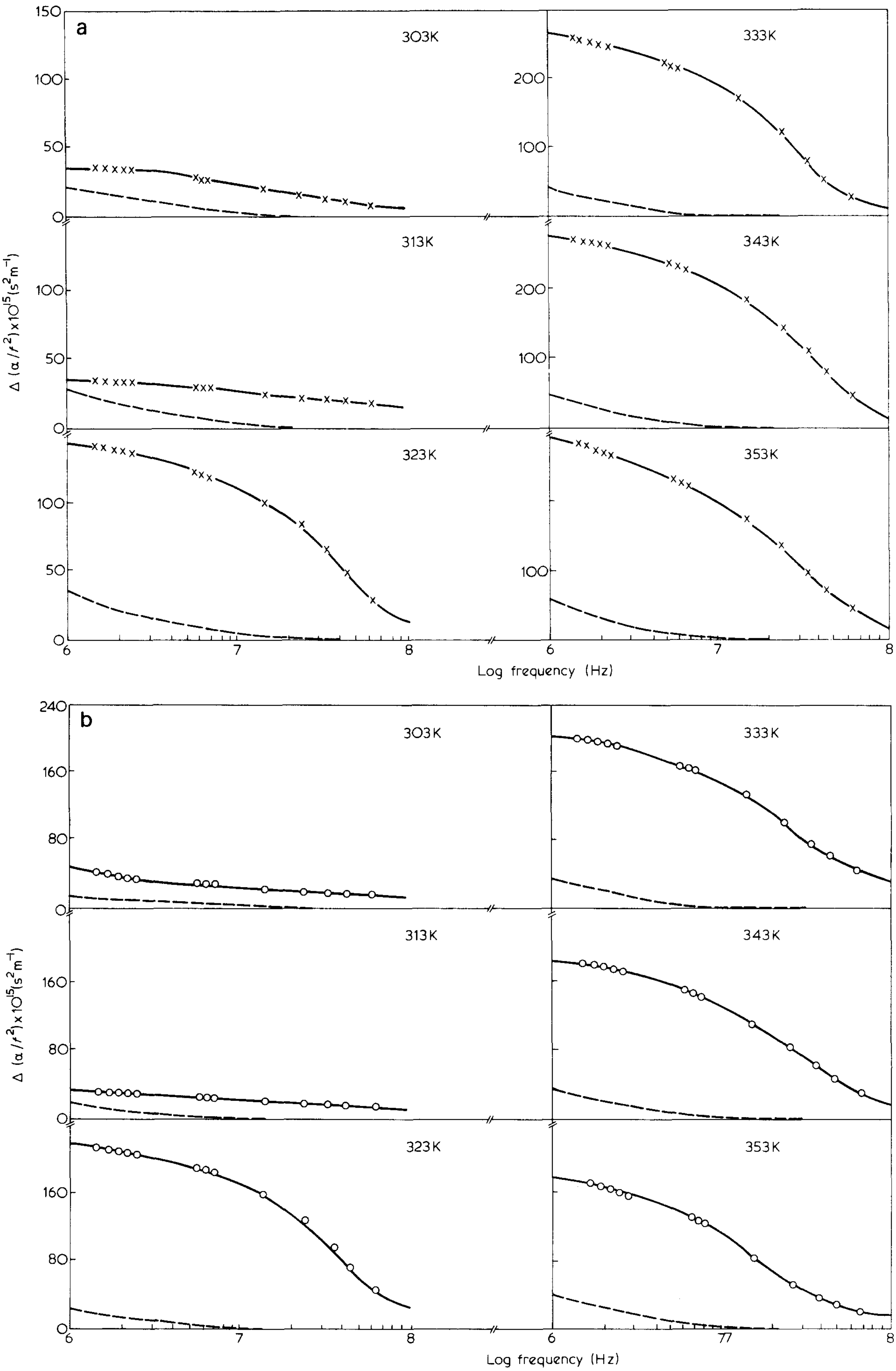


Figure 2 Ultrasonic dispersion data at various temperatures for poly(isobutylene) in xylene (4% w/v). a, Vistanex L80, $M_n = 4.22 \times 10^3$; b, Vistanex L140, $M_n = 6.11 \times 10^5$. Symbols represent experimental points. Lines are curves calculated as described in the text — — —, Viscoelastic contribution

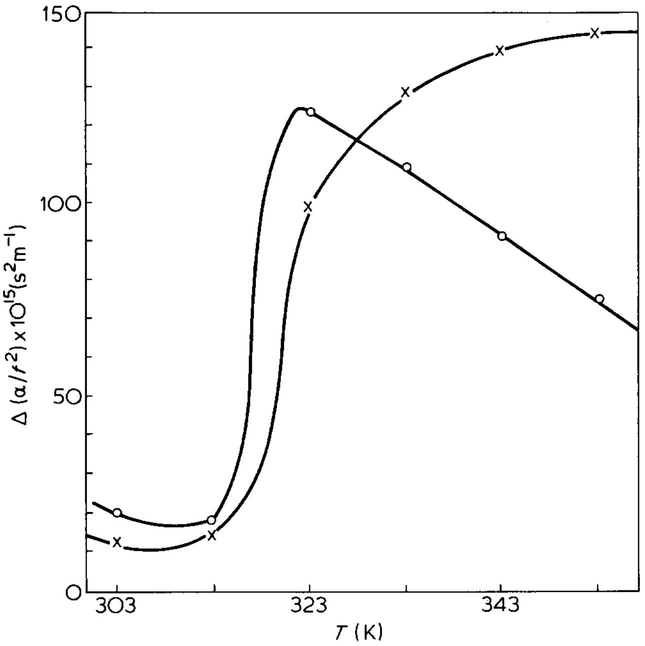
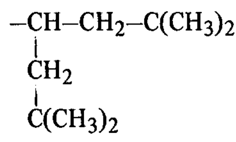


Figure 3 Variation of acoustic absorption as a function of temperature at 25 MHz for poly(isobutylene) in *m*–xylene (4% w/v). X, Vistanex L80; O, Vistanex L140

The spectrum of the L140 sample shows a clearly distinguishable peak at $\tau = 7.95$ which can be attributed to the occurrence of a tertiary carbon resulting from the creation of chain branches. Proton rearrangement during cationic polymerization can lead to the structure:



$$-\underset{\underset{\underset{C(CH_3)_2}{|}}{CH_2}}{\underset{|}{CH}}-CH_2-C(CH_3)_2-$$

Analar grade *m*-xylene was used as the solvent. Prior to use, *m*-xylene was redistilled, dried over molecular sieves and filtered with micropore filters. A 4% w/v solution of each polymer sample was then prepared and allowed to dissolve completely before any measurements were made.

RESULTS AND DISCUSSION

Analysis of data

As in the studies of other polymer solutions[37,39] it is assumed that the observed ultrasonic relaxation spectrum is a composite of normal mode and segmental relaxation processes. The viscoelastic contribution was calculated using the theory of Wang and Zimm[40]. Viscoelastic measurements on comparable solutions have indicated that the polymer behaves as though it is in the free-draining limit, and so eigenvalues appropriate to this case were used in the calculation of the absorption response function. The conformational absorption, obtained as the difference between the calculated normal mode contribution and the total observed value was fitted to a Cole–Cole[41] distribution function as described elsewhere[38,39]. In all cases the error between the fitted and observed curves was less than ±1% (*Figure 2*).

A marked increase in the total absorption with increasing temperature was observed (*Figure 3*). As before, we ascribe this to the collapse of ordered chain sequences which, at lower temperatures, are unable to participate in the conformational relaxation. By introducing a single parameter, n, describing the number of rotors 'trapped' in the ordered or helical sequence at low temperatures, a self-consistent picture of the relaxation energetics can be obtained.

The interstate enthalpy was computed assuming that the mean parameters for a simple rotational isomeric process are involved in the observed relaxation. With the single rotor concentration parameter it is possible to obtain linear plots of $(\mu_m/Tc^2)^{1/2}$ where μ_m is the maximum absorption per unit wavelength and c is the sound velocity (*Figure 4*). A surprising feature of this analysis is that the plots for the two polymers have slopes of opposite sign. For the Vistanex L80, the interstate enthalpy was obtained from a plot of $\log(T\mu_m/c^2)$ *versus* $1/T$, the slope of which yields ΔH^0 directly. In the case of L140, in which $(\mu_m/Tc^2)^{1/2}$ decreases with increasing temperature, it is not possible to use the analysis described above. The two polymers must have slightly different values of ΔG^0, such that at the temperatures of the experiment, the values of $\Delta H^0/RT$ lie on opposite sides of the maximum in the Schottky curve (relaxation amplitude or relaxing specific heat plotted against $\Delta H^0/RT$). The temperature coefficient in this case implies that the system lies on the low $(\Delta H^0/RT)$ side of the maximum. It is then possible to obtain ΔH^0 if an assumption is made about ΔS^0 by calculating the quantity:

$$F = (2JC_p^2/\pi R\theta^2\rho V)^{1/2}(\mu_m/Tc^2)^{1/2}$$

from the experimental results and comparing this with values predicted for various trial values of $\Delta H^0/RT$. J is the mechanical equivalent of heat, θ is the thermal expansion coefficient, V is the molar volume, c is the velocity, ρ is the density and C_p the specific heat of the propagating medium.

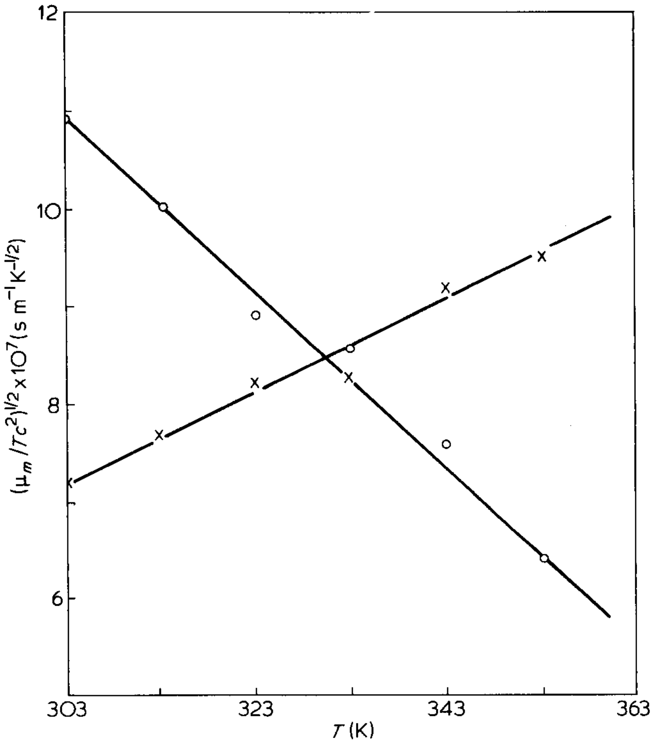


Figure 4 Variation of $(\mu_m/Tc^2)^{1/2}$ as a function of temperature for poly(isobutylene) solutions (4% w/v). X, Vistanex L80; O, Vistanex L140

Table 1 Conformational relaxation parameters for poly(isobutylene) solutions (4% w/v) at various temperatures

Solution	*T* (K)	*A* × 10^{15} ($s^2 m^{-1}$)	*fc* (MHz)	*β*
L80/*m*—xylene	303	20	24.3	0.80
	313	15	25.2	0.77
	323	110	34.0	1.00
	333	194	25.0	1.00
	343	225	35.0	1.00
	353	235	30.0	1.00
L140/*m*—xylene	303	20	13.5	0.78
	313	13	16.0	0.80
	323	185	34.5	1.00
	333	170	34.0	1.00
	343	150	30.0	1.00
	353	138	18.8	0.90

Table 2 Density, viscosity and acoustic velocity of polyisobutylene solution (4% w/v) in *m*—xylene

Solution	*T* (K)	Density (x10^{-3} kg m^{-2})	Viscosity (x10^3 Ns m^{-2})	Velocity (m s^{-1})
L80/*m*—xylene	303	0.8572	67.92	1331
	313	0.8498	61.41	1269
	323	0.8399	54.10	1220
	333	0.8325	48.62	1190
	343	0.8338	43.70	1153
	353	0.8181	40.00	1105
L140/*m*—xylene	303	0.8588	1003	1330
	313	0.8502	900.9	1269
	323	0.8396	774.7	1223
	333	0.8330	726.7	1185
	343	0.8345	659.6	1145
	353	0.8210	571.4	1099

We have assumed $\Delta S^0 = R \ln 2$, implying two-fold degeneracy in the higher conformational state. This introduces a slight uncertainty in ΔH^0, but in this region ΔH^0 is not very sensitive to the value of ΔS^0.

The values of ΔH^0 obtained are 6.5 kJ mol^{-1} for Vistanex L80 and 4.9 kJ mol^{-1} for Vistanex L140. Relaxation parameters for the two polymers are presented in *Table 1*.

Vistanex L80

At low temperatures (*Figure 3*), the absorption is determined essentially by the viscous losses and a small contribution from conformational change. An increase in temperature is accompanied by a decrease in viscosity (*Table 2*) and a corresponding reduction in the acoustic velocity. These observations invalidate the hypothesis of previous workers that the increased absorption is due to the formation of an entangled network structure. In line with the interpretation of n.m.r. measurements^{25} we propose that the marked increase in the absorption above 313K is associated with an increase in the number of relaxing units due to a pseudo helix—coil transition of the polymer backbone. A similar phenomenon has been observed in polystyrene solutions. In this case the backbone substitution is symmetrical, and hence the helical structure is generated as a consequence of the 1—3 interactions of the methyl groups on neighbouring monomer units. The number of relaxing units (estimated from the change in the absorption amplitude assuming the conformational energy difference is unaltered by the process), is approximately 14, twice as many as involved in the corresponding transition in polystyrene.

Vistanex L140

In this polymer the amplitude reaches a maximum and then decreases as the temperature is increased. There is no corresponding change in the viscosity, confirming that the relaxation is primarily conformational in origin. In this case the number of rotors immobilized at low temperatures is somewhat smaller, approximately 5. This can be ascribed to the irregularity detected by n.m.r.

The difference in the temperature dependence of the amplitude is also a consequence of the change in the type of unit involved in the relaxation. The occurrence of H-shift branch units in the backbone significantly reduces the steric interactions between neighbouring methyl groups, and so provides a mobile link in the backbone. Such a structural defect will involve side chain motion in addition to that of the backbone, and this is reflected in the change in the temperature dependence of the absorption and lower enthalpy difference between conformational states.

Sound velocity and adiabatic compressibility

The adiabatic compressibilities (obtained from the sound velocities) of both solutions were lower than those of the solvent at all temperatures (*Figure 5*). The more rigid L80 is less compressible than the L140, probably because of reduced ease of access of the solvent to the polymer back-

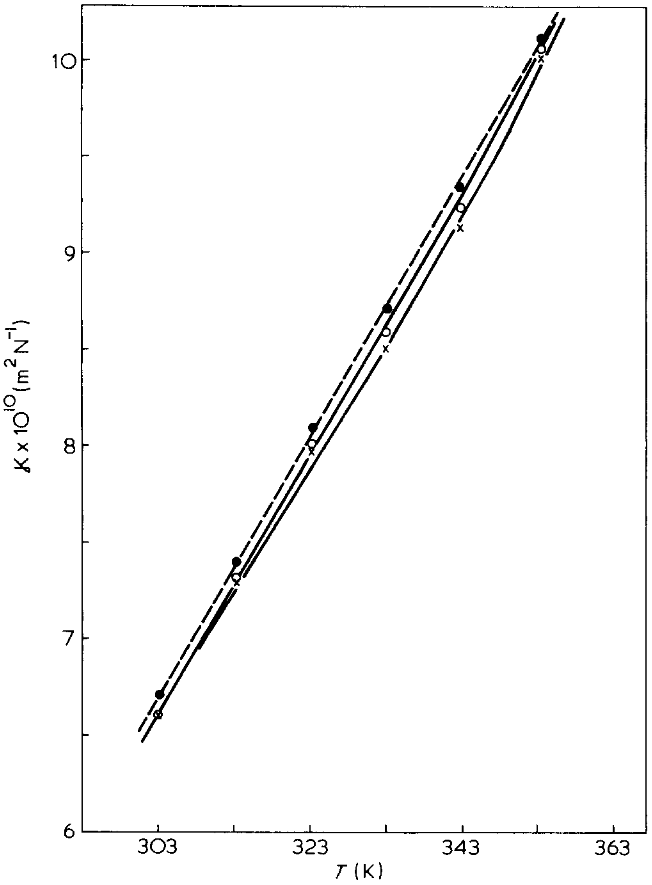


Figure 5 Variation of adiabatic compressibility as a function of temperature for *m*—xylene and poly(isobutylene) solutions (4% w/v). ●, *m*—xylene; X, Vistanex L80/*m*—xylene; ○, Vistanex L140/*m*—xylene

bone. Thus the whole picture is self-consistent in the way differences in absorption and velocity arise from differences in chain regularity and branching.

ACKNOWLEDGEMENTS

The authors acknowledge the assistance of the SRC in provision of equipment used in these studies, and also wish to thank Esso Chemical Company Ltd for the gift of the polymers used. BTP wishes to thank the University of Science, Malaysia, for financial assistance for the period of the research programme.

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