Molecular motion in α-methylstyrene and styrene–alkane copolymers studied by ^{13}C n.m.r. spectroscopy

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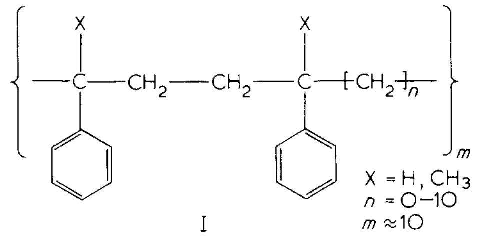
The temperature dependence of the ^{13}C n.m.r. relaxation times are reported for a series of copolymers formed between methyl styrene or styrene and various α, ω-alkyl dihalides. The polymers studied contained alkyl blocks with n (the number of CH_2 units) varying from 0–10. The relaxation data indicates that the motion of both the styrene and the alkyl blocks change with the value of n. A comparison of the ^{13}C relaxation data with that obtained from ultrasonic relaxation measurements supports the hypothesis that in the higher members of each series the alkane chain moves essentially independently of the 'styrene' moiety. The variation in the activation energy of the relaxation of the styrene moiety reflects in part a decoupling of the neighbouring phenyl group motion, as a consequence of the introduction of the alkane block.

INTRODUCTION

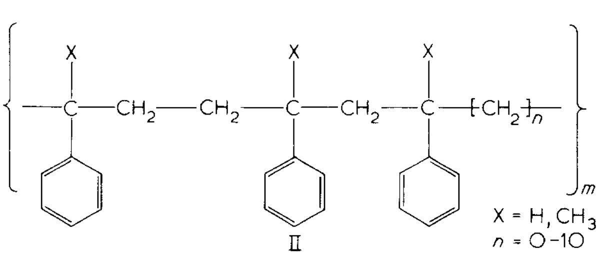
In recent years ^{13}C n.m.r. spectroscopy has made a significant contribution to both the study of sequence structure in polymers[1–6] and also as a probe of molecular motion[7,8]. Although much less sensitive than ^1H n.m.r., the ^{13}C technique has a number of important advantages over the former in the study of polymer dynamics. Use of ^1H decoupling usually leads to a spectrum which consists of single lines, uniquely defining the structural sequences present in the polymer and relaxed via dipolar interactions through the attached protons. The internal motions of the polymer have correlation times which are usually greater than 10^{-11} s and dominate the spectral distribution at the Larmor precession frequency.

One of the principle problems associated with the analysis of the relaxation data in polymeric materials is the construction of a realistic model for the description of the relaxation process. In a chain molecule the motion of an individual carbon atom may be expected to be coupled to its neighbours to an extent which depends on the form of the intramolecular potential and the range of the forces involved. A study of the α-methylstyrene and styrene–alkane copolymers provides an ideal system for an investigation of correlation in the motion of units along a polymer backbone. In a previous paper[9], the authors discussed an assignment of the ^{13}C n.m.r. spectrum of the α-methylstyrene–alkane copolymers based on the spectra of the related pentyl dimers. The copolymers were shown to conform to the general structure I:



I

Detailed studies of the copolymers formed with varying ratios of α-methylstyrene to α,ω-alkyl dihalide in the polymerization mixture[9] enabled the spectral characteristics of the structure II to be identified:



II

All the copolymers used in these relaxation studies have less than 5% of structure II. A previous ultrasonic relaxation study of these copolymers[10] indicated that the motion of the α-methylstyrene or styrene moiety was a function of the size of the alkane block, the rate of reorientation increasing with the value of n. It was not possible from the ultrasonic studies to observe the motion of the alkane block. The ^{13}C n.m.r. technique

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Table 1 Molecular weights of copolymers

Values $M_n \times 10^{-3}$	Value of n (no. of CH_2 units per block)						
Series	1	2	3	4	5	6	10
Styrene	2.06	2.12	1.98	3.64	2.38	2.39	1.93
α-Methylstyrene	1.20	1.83	1.51	2.46	1.78	1.81	2.13

not only allows study of all the nuclei in the polymer but also provides data with which the ultrasonic relaxation may be compared.

It has been established by a number of workers[11-17] that the ^{13}C, T_1 values for polymers in solution are intimately connected with the internal motions of the chain backbone. A detailed interpretation of the data requires consideration of a molecular model interrelating the observed T_1 values and the motion of specific nuclei. In a polymer system consideration of the effects of coupling on the motion of specific sites leads to the suggestion that a distribution of relaxation times should be observed[17]. Coupling of the motion is, however, not the only mechanism whereby a distribution of relaxation times may arise. In this study, comparison will be made of the values of T_1 in a series of closely related chemical structures of essentially the same molecular weight and solubility, hence excluding variations arising from molecular weight dependent and solvent interaction effects. In an attempt to identify the range of coupling of the motion, evidence from ultrasonic measurements will be correlated with the ^{13}C observations.

EXPERIMENTAL

Copolymer preparation

Full experimental details of the preparation of the copolymers are given elsewhere[18,19]. In a typical reaction about 1.0 mol lithium in 500 ml of tetrahydrofuran (THF) was stirred under nitrogen in a one litre three necked flask. A mixture of α-methylstyrene or styrene (0.4 mol) and alkyl dihalide (0.2 mol) in THF was added, and the solution stirred for several hours, reaction temperature being maintained at 0°C. The polymer was precipitated from methanol, purified by reprecipitation and dried in a vacuum oven at 60°C. The molecular weights were determined using a Waters Associates gel permeation chromatograph[20], *Table* 1.

^{13}C n.m.r. relaxation measurements

The ^{13}C spin lattice relaxation times were measured using the standard π, t, $\pi/2$ pulse sequence. Measurements were made at 22.6 MHz on a Bruker HX-90E spectrometer at PCMU, Harwell, and at 25MHz on a Varian XL-100 spectrometer at the University of Manchester and JEOL PFT-100 spectrometers at PERME and the University of Strathclyde.

The measurements were performed on approximately 25% w/v solutions in $CDCl_3$, the solvent providing the internal ^2H lock signal. Because the molecular weights of the polymers are low effects due to entanglement need not be considered in the interpretation of the data. Similarly the high viscosity of the solution leads to the prediction that 'normal' mode motions would lie well below the frequency domain of interest in the ^{13}C experiments. Internal checks revealed no significant difference between the data obtained on the various instruments used. Both manual and automatic data collection procedures were used. The values of T_1 presented in this paper are averages of the values obtained from different experiments.

Initial observations of the spectral changes during the standard pulse sequence produced modulation effects when the pulse delay t was comparable with T_2. The cause of this phenomenon was finally established by the use of a spoiling pulse immediately after the initial 180° pulse. The spoiling pulse destroys the field homogeneity in the xy plane and eliminates complications which arise from free induction decay of a residual component of the 180° pulse when the 90° pulse is applied. These effects will only be observed when τ and T_2 are comparable. The spectra obtained using the spoiling pulse enabled relaxation times to be obtained for these copolymers.

RESULTS AND DISCUSSION

Assignment of ^{13}C spectra for the styrene–alkane polymers

In the previous paper[9], an assignment was reported for the α-methylstyrene–alkane copolymers. The assignment of the styrene–alkane series has not been so far reported and a similar approach to that adopted previously[9] was followed here. Grant and Paul[23] have proposed that the chemical shift of a particular carbon atom (δ_c^i) is given by a simple additive equation of the form:

$$\delta_c^i = B + \sum_j A_j N_{ij} \qquad (1)$$

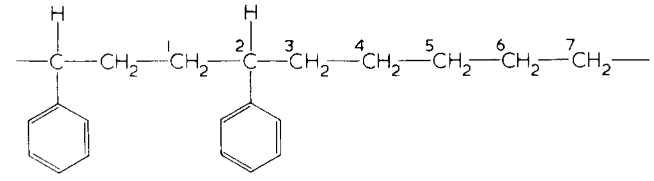
where A_j has characteristic values for carbon atoms α, β, γ, δ and ε relative to the ith carbon atom and N_{ij} is the number of carbon atoms with coefficient A_j. The values of the constants used in the computation of the δ_c^i for the copolymers are summarized in *Table* 2.

The doublet splitting of the phenyl quaternary carbon was once more observed in the styrene series and attributed to the steric configurations of the styrene units. Comparison of the computed spectra based on equation (1), with the observed, *Table* 3, indicated that the principle features of the spectrum can be adequately explained in terms of the structure shown. Close inspection of the spectrum indicates that

Table 2 Constants used in the calculation of chemical shift data. When $\delta_c{}^i$ is the shift relative to TMS, B has a value of −2.6 ppm and A_j takes the following values

Carbon atom j	α	β	γ	δ	ε
A_j (carbon)	+9.1	+9.4	−2.5	+0.3	+0.1
A_j (phenyl)	+23	+9.5	−2		

Table 3 Peak positions for Styrene–alkane copolymers

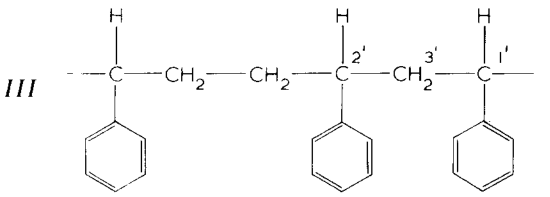


Copolymer		C_1	C_2	C_3	C_4 (ppm relative to TMS)	C_5	C_6	C_7
Propane	Calc	35.3	46.0	37.3	25.8			
	Obs	35.9 35.7 35.1 34.8	46.5 46.4	37.5 37.9	26.0			
Butane	Calc	35.3	46.0	37.3	27.8			
	Obs	35.19 34.41	46.4 45.9	37.1 36.7	27.6			
Pentane	Calc	35.3	46.0	37.3	27.8	30.0		
	Obs	35.3 34.3	46.44 45.93	37.3 36.8	27.5	29.8		
Hexane	Calc	35.3	46.0	37.3	27.8	30.0		
	obs	35.3 34.4	46.45 46.0	37.3 36.8	27.6	29.6		
Decane	Calc	35.3	46.0	37.3	27.8	30.0	29.9	30.4
	Obs	35.0 34.2	46.2 45.8	36.9 36.7	27.5	29.5	29.5	29.5

N.B. The observation of a doublet structure in the ^{13}C spectra indicated by the assignment of two peaks to a single predicted line indicates the possibility of differences in tacticity of the styrene moiety of the copolymer

peaks are also observed at 42.9–43.0 ppm consistent with the occurrence of trimer sequences of the form:

III



the additional peaks being assigned to the C_1' and C_2' carbon atoms. The C_3' carbon atom is also expected to occur in this region and can be assigned to a weak feature at 44 ppm. The spectrum of the styrene–butane copolymer shows a strong peak at 40.6 ppm which is additional to those expected from the above structure. The peak is close to a similar feature observed in the homopolymer styrene at 40.7 ppm and assigned to the backbone carbon to which the phenyl ring is attached. This would suggest that the butane sample contains a number of head-to-tail styrene sequences, which is in contrast to the structure found in the other copolymers. It should be mentioned that the doublet structure observed for many of the aliphatic resonances can be ascribed to the occurrence of two different configurations for each of the above structures.

Table 4 Typical values of the relaxation times observed at 293K

Polymer	Carbon atom (Ms) C_1	C_2	C_3	C_4	C_5	C_6	C_7
Styrene–butane	70	125	80	70	–	–	–
Styrene–docane	60	165	115	85	165	165	165
α-Methylstyrene –butane	65	125	75	70	–	–	–
α-Methylstyrene –decane	70	120	95	80	90	90	90

Analysis of relaxation data

The spin lattice relaxation times (T_1) were obtained from plots of the signal intensity *versus* time using the equation:[24]

$$M_t = M_\infty(1 - 2e^{(-t/T_1)}) \tag{2}$$

where M_t and M_∞ are respectively the intensities at time t and the equilibrium value of the proton decoupled spectra recorded using the pulse sequence described above. Typical values of the relaxation times are listed in *Table* 4. The observation of the approximate factor of two between CH_2 and CH ^{13}C relaxation times indicates that the extreme narrowing limit can be applied to these motions.

The Nuclear Overhauser Enhancement Factor *NOEF* was determined using the transient method[25] The linearity of these plots over virtually the whole measured timescale is consistent with a single relaxation time. The *NOEF* values obtained were close to the theoretical value for dipole–dipole relaxation and close to those reported for the appropriate homo-

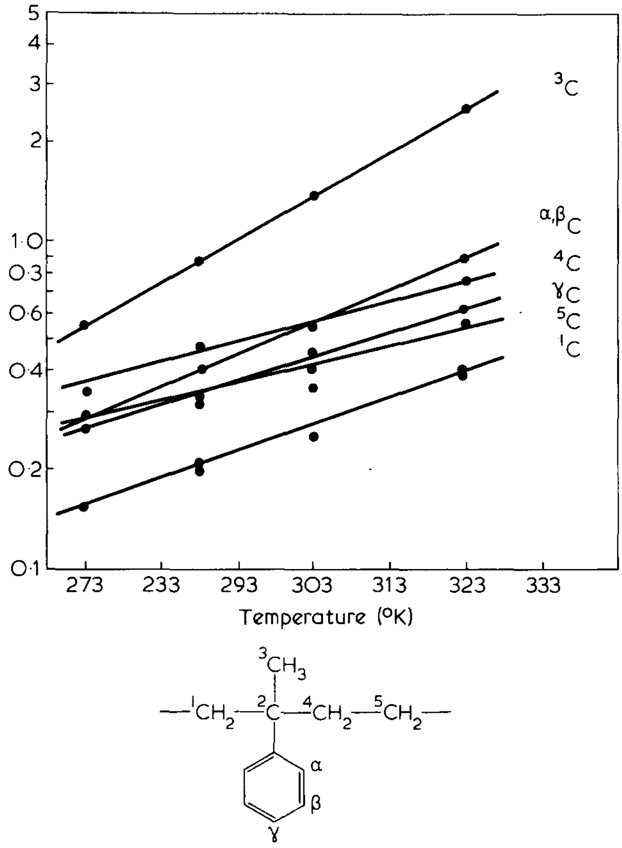


Figure 1 Variation of T_1 for α methyl styrene-butane with temperature

polymers[26,27]. This confirms the hypothesis that the spin lattice relaxation in these polymers is dominated by the dipolar mechanism.

A detailed analysis of the T_1 data relies on the use of a model to translate the observed ^{13}C relaxation data into a picture of the molecular motions which occur in the copolymer. The motion of the copolymer will be artificially sub-divided into three sub-groups; methyl top motion, styrene moiety isomerism and alkane group relaxation. Of these motions the simplest and most easily analysed is that of the methyl top. The form of the correlation functions and the method of analysis has been discussed in detail by Woessner[28] and was followed here.

For the remaining nuclei, relaxation may be expected to occur by a combination of short range torsional motions, internal rotation and overall rotation of the whole polymer. The complexities which arise from these various contributions have been discussed in detail for the motions of an analogous system of normal hydrocarbons[29,30] and 2-methyl nonadecane[31,32]. For medium and low molecular weight chains, the observed T_1 depends upon the overall tumbling motions of the entire chain. In this situation we can define an effective correlation time of the *i*th carbon as:

$$(\tau_{\mathrm{eff}}(i))^{-1} = \tau_0^{1} + \tau_{\mathrm{int}}(i)^{-1} \qquad (3)$$

where $\tau_{\mathrm{eff}}(i)$ is the effective correlation time of the *i*th carbon, τ_0 is the rotational correlation time of the entire chain and $\tau_{\mathrm{int}}(i)$ is that part of the effective correlation time which can be associated with internal motion of the *i*th carbon. It has been shown that the difference in effective correlation times of neighbouring atoms is a direct method of obtaining information on the effects of various intramolecular interactions on the rates of internal rotation of specific molecular entities[33]. The effective correlation time, in the extreme narrowing limit τ_{eff} can be calculated from the dipolar contribution to T_1 by

$$\tau_{\mathrm{eff}} = r_{\mathrm{CH}}^6 / K T_1(D) n_H \qquad (4)$$

where r_{CH} is the internuclear distance (1.09 Å for aliphatic C–H bonds), $T_1(D)$ is the dipolar spin lattice relaxation time, n_H is the number of attached protons and K is a constant equal to 3.56×10^{10} Å^6 s^{-2}.

In the following analysis, an average correlation time for the styrene and alkane moieties was calculated. It was found in practice, that the correlation times for all the atoms forming part of a particular moiety were very similar. In this paper no attempt will be made to separate the various librational and torsional motions which can be assigned to the phenyl group. It should, however, be noted that the T_1 s for the α, β and γ carbons are larger than those for the associated methine carbon. Also the T_1 s for the γ arbons are clearly shorter than for the α and β carbons; both these facts can be explained on the basis of limited librational and phenyl group rotatory motions.

It was found experimentally that for the copolymers with short alkane chains, the τ_{eff} of the styrene and alkane moieties were identical within experimental error. Increasing the size of the alkane block leads to a situation where distinct differences are observed between the τ_{eff} of styrene and alkane blocks. In this case the τ_{eff} of the styrene moiety was taken as the mean of the methine and phenyl group motions and that of the alkane as being the mean of the τ_{eff} of the carbons furthest from the phenyl group. In the case of the decane polymer, the carbon atoms forming the central portion of the alkane block C^5–C^7 exhibited identical τ_{eff}.

The activation energy for a thermally activated rotational isomeric process may be described by[34]

$$\tau = A \exp(-\Delta E/RT) \qquad (5)$$

Hence plots of the τ_{eff} against reciprocal temperature yield an apparent activation energy for the process being proved.

Discussion of data

The copolymers were studied over the temperature range 273 to 323K. Logarithmic plots of T_1 against temperature for the copolymers with *n* less than or equal to four were observed to be essentially linear, *Figure* 1. The calculated correlation times using equation (7) showed a similar linear dependence when plotted against reciprocal temperature and allowed mean activation energies to be calculated, *Table* 5. Similar plots for higher members 1, $n > 4$, were markedly nonlinear, *Figure* 2, and the values of ΔE obtained for these polymers correspond to a best fit of the data over the available temperature range.

(i) *Methyl group rotation.* The values of the activation energies for methyl group rotation obtained

Table 5 Activation parameters for copolymers (ΔE kJ mol^{-1})

	Me group motion	Styrene moiety motion	Alkane moiety motion	Acoustics[10]
Copolymer				
α-Methylstyrene				
—homopolymer	28.2	38.2	–	36.8
—methane	–	–	–	32.9
—butane	26	30.7	27.8	–
—pentane	24	28.2	20.4	–
—hexane	19	26.5	14.2	23.2
—decane	17	24.4	11.2	22.4
Styrene				
—homopolymer	–	–	–	29.2
—methane	–	–	–	25.9
—butane	–	23.8	22.2	24.9
—hexane	–	18.0	12.6	17.0
—decane	–	17.6	10.2	15.7

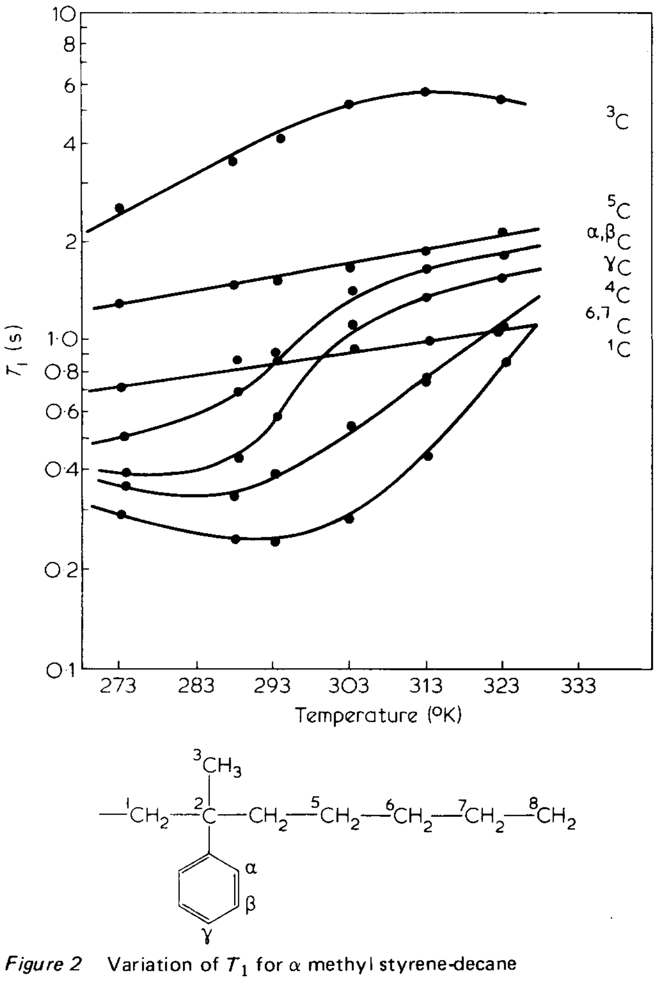


Figure 2 Variation of T_1 for α methyl styrene-decane

from this study are similar in magnitude to those obtained from neutron scattering and proton relaxation studies[41–51], *Table* 6. The value obtained for the α-methylstyrene homopolymer is slightly lower than that reported for the heterotactic polymer but significantly higher than that for the head-to-head polymer. This observation would suggest that the occurrence of a proportion of head-to-tail as well as head-to-head sequences leads to a higher activation energy in the polymer studied in this paper than in the purely head-to-head polymer. The gradual decrease in the activation energy with increasing value of n, *Figure* 3, reflects an increased ease of internal rotation with increased styrene moiety separation.

(*ii*) *Styrene moiety motion* The lower members of both series exhibit a rotational isomeric process with an activation energy of ~30–40 kJ mol^{-1}, similar to that reported for polystyrene[29]. Increase in the alkane chain length leads to a decrease in the activation energy for rotational isomerism, paralleling the acoustic studies[10], *Figure* 3. The similarity in the variation of the activation energy for the methyl group and styrene moiety motion with increasing alkane chain length indicates that the motions are cooperative. This hypothesis is also consistent with the observed changes in the pre-exponential factor of equation (5), which reflects differences in the order and number of vibrational states involved in achieving a particular activation state.

The non-linearity of the plots for both the hexane and decane copolymers, correspond to similar changes reported in polystyrene at ~343K[29]. In this case the changes in slope are attributed to an increased ease of internal rotation associated with enhanced phenyl group motions. A similar hypothesis may explain the trends observed in this study, however a detailed picture of the individual motions is not readily obtained from this data.

Table 6 Activation energies and barriers for methyl motion

	E_a (Arrhenius) (kJ mol^{-1}	V_3
Poly(propylene)	12.1[35]	12.5[36]
Poly(propylene oxide)	15.9[38,39]	18.4[37,40]
Poly(methyl methacrylate)		
α-Me rotation syndiotactic	24[41,43]	28.9[37]
α-Me rotation isotactic	15.5[41,43]	16.7[37]
—OCH$_3$ all isomers	very low	4.2[37]
Poly(α-methylstyrene)	–	37[42]
Syndiotactic/heterotactic		
Head to head	–	23[42]
Poly(dimethyl siloxane)	–	6.9[42]
Poly(4-methyl pentene-1)	–	15[42]
Poly(alkane) linear	–	11[29]
2-Methyl doplecane branched	–	12[29]

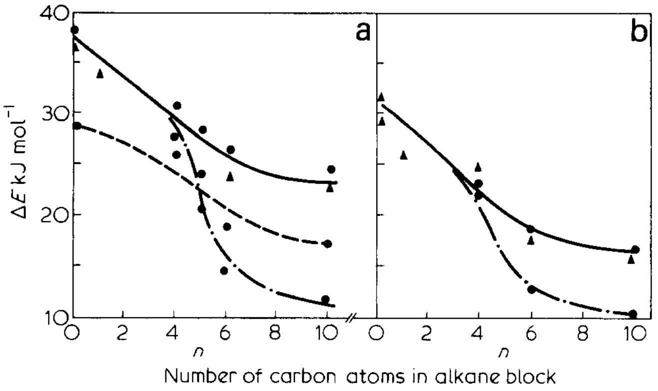


Figure 3 Activation energy plots for the copolymers; (a) α methyl styrene-alkane; (b) styrene-alkane. ——, styrene motion; — · — · —, alkane motion; — — — —, methyl motion; ▲, acoustic; ●, ^{13}C n.m.r.

(iii) Alkane group motion In the shorter chain alkane copolymers $n < 4$ the relaxation of the alkane block is indistinguishable from that of the styrene moiety indicating the coupled nature of the motion, *Figure* 3. Independent motion of carbon atoms in the alkane block does however appear possible when $n > 6$. The value of the activation energy for the alkane block motion in the decane polymers are close to those reported from n.m.r.[31-33] and acoustic studies[44] of the lower alkanes.

CONCLUSIONS

The nature of the relaxation which occurs in these polymers is not only a function of the alkane chain size but also of the temperature range of observation. In the longer chain copolymers decoupling of the alkane motion is possible. However, the motion in the shorter chain copolymers reflects a highly cooperative motion. The involvement of the methyl group in the internal rotation of the styrene moiety is indicated from the observed parallelism in the variation of both relaxation processes with increase in chain length. Comparison of the activation energies for the styrene and α-methylstyrene indicates that the presence of the methyl group increases the energy by ~ 6 kJ mol^{-1} which is similar in magnitude to the effect observed on substitution of two protons by methyl groups on a hydrocarbon backbone[45]. The idea that coupling occurs over a number of monomer units is consistent with recent theories of polymer relaxation[5,8] and supports the use of the simplified analysis adopted in this paper.

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