

# Dynamics of molecular chains. Ultrasonic relaxation of monosubstituted polystyrenes

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(Received 23 January 1979; revised 3 April 1979)

The ultrasonic attenuation of polystyrene derivatives: *o*-(CH<sub>3</sub>, Cl, Br), *m*-(Br), *p*-(Br) and  $\alpha$ -methyl, has been investigated as a function of temperature and frequency. At least two relaxation processes were needed to account for the ultrasonic spectra and the related thermodynamic parameters have been calculated. The position and steric hindrance of the substituent have no significant effect on the activation energy but affect the enthalpy difference corresponding to the highest frequency relaxation process. The results obtained permit comparison of the intramolecular mobility of the monosubstituted polystyrenes with that of polystyrene. Poly( $\alpha$ -methylstyrene) behaves very much like polystyrene. Intramolecular mobility appears higher in poly(*m*-bromostyrene) than in *p*- or *o*-substituted polymers. Finally, the shift of the ultrasonic spectra of *o*-substituted polystyrenes to low frequencies is all the stronger as the substituent is bulky.

## INTRODUCTION

Polystyrene derivatives obtained by introducing a substituent either at the  $\alpha$  position on the main chain, or on the phenyl ring, are particularly suitable for studying the influence of steric hindrance on the various motions which can be identified, such as segmental reorientation and internal rotation of the phenyl group. Results obtained from <sup>13</sup>C nuclear magnetic relaxation<sup>1,2</sup> have permitted comparison of the intramolecular mobility of monosubstituted polystyrenes with that of polystyrene. Poly( $\alpha$ -methylstyrene) does not differ from polystyrene except for a slight slowing of both segmental reorientation and internal phenyl group motions and apparent hindrance of the methyl group rotation. Reorientation of the chain backbone and internal motion of the side-chain rings are both slowed by the replacement of the hydrogen atom at the *ortho* position of the phenyl ring by CH<sub>3</sub> group, F, Cl or Br atom. This *ortho* effect is all the stronger as the substituent is bulky. On the other hand, for *meta* or *para* substitution, relaxation times do not depend on the substituent. Although the relaxation times of aromatic carbons are equal to *m*- and *p*-halogenated derivatives, with respect to the aliphatic carbons, intramolecular mobility seems higher in *m*-substituted polymers.

Dielectric dispersion measurements on dilute solutions of polar chain molecules offer a principal means of studying short range or 'local' modes of chain motion. Dielectric loss measurements from 5 to 150 MHz are reported in the literature for polymers of several styrene derivatives in benzene or toluene solutions. For poly(*p*-chlorostyrene)<sup>3-5</sup> and poly(*p*-bromostyrene)<sup>3</sup> the frequency of maximum dielectric loss is about 30-40 MHz and the apparent activation energies are 4.8 kcal/mol and 3.2 kcal/mol, respectively. The main difference between the dielectric measurements of *p*- and *m*-chlorinated<sup>6</sup> or fluorinated<sup>5</sup> polystyrenes is a relaxation

frequency shift. The slightly higher relaxation rate of *m*-substituted polystyrenes as compared with the *p*-substituted polystyrenes may be attributed either to the phenyl group reorientation about the C<sub>1</sub>-C<sub>4</sub> axis or to an higher mobility of the chain backbone.

In order to supplement the dynamic analysis of these polymers, the ultrasonic attenuation of polystyrene derivatives: *o*-(CH<sub>3</sub>, Cl, Br), *m*-(Br), *p*-(Br) and  $\alpha$ -methyl, has been investigated as a function of temperature and frequency. The ultrasonic spectra and the related thermodynamic parameters will be given in the first part of this paper. The second part will be devoted to the relationship between chemical structure and intramolecular mobility.

## EXPERIMENTAL

### Samples

Poly(*p*-bromostyrene) was supplied by EGA-Chemie and had a number-average molecular weight of 14 000. Poly( $\alpha$ -methylstyrene) was prepared by cationic polymerization at -78°C with BF<sub>3</sub>OEt<sub>2</sub> as catalyst and had a number average molecular weight of 336 000. *O*-substituted polystyrenes and poly(*m*-bromostyrene) were prepared by free-radical polymerization at 60°C with AIBN as the initiator. The molecular weights are as follows:

Polymer	$\bar{M}_n$
<i>o</i> -methyl	$8.53 \times 10^4$
<i>o</i> -chloro	$2.66 \times 10^5$
<i>o</i> -bromo	$3.8 \times 10^5$
<i>m</i> -bromo	$4.0 \times 10^5$

0032-3861/78/080990-05\$02.00

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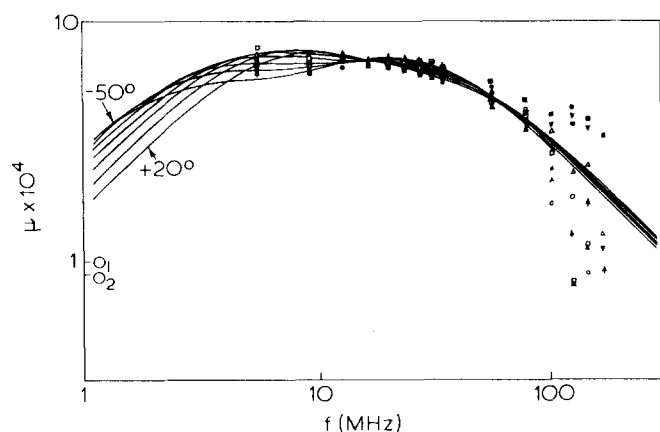


Figure 1 Ultrasonic relaxation spectra of poly(*o*-methylstyrene) in ethylbenzene. Concentration:  $5 \times 10^{-2} \text{ g cm}^{-3}$  (origin  $O_1$ );  $4.81 \times 10^{-4}$  monomer units per  $\text{cm}^3$  (origin  $O_2$ )

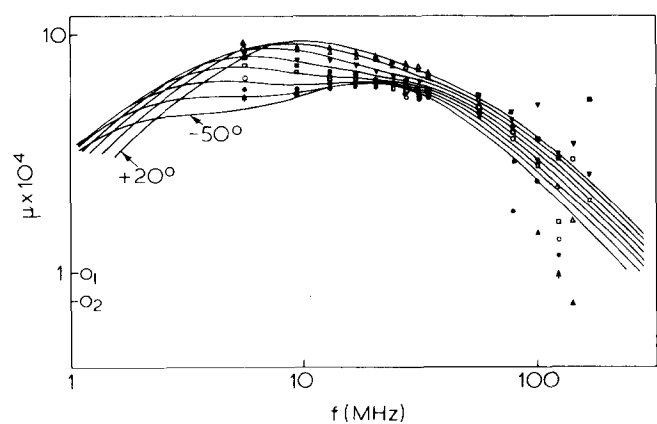


Figure 2 Ultrasonic relaxation spectra of poly(*o*-chlorostyrene) in ethylbenzene. Concentration:  $5 \times 10^{-2} \text{ g cm}^{-3}$  (origin  $O_1$ );  $4.81 \times 10^{-4}$  monomer units per  $\text{cm}^3$  (origin  $O_2$ )

The polydispersity indices are close to 2. The polymers were thoroughly dried *in vacuo* at  $60^\circ\text{C}$  for at least 24 h.

#### Ultrasonic experiments

With the exception of poly(*p*-bromostyrene), ultrasonic experiments were carried out in the temperature range  $-50$  to  $+20^\circ\text{C}$  on 5% w/v ethylbenzene solutions. The absence of polymer precipitation as temperature decreased was checked by light scattering. In the case of poly(*p*-bromostyrene), which cannot be dissolved in ethylbenzene, experiments were performed on 5% w/v toluene solutions at  $+20^\circ$  and  $+30^\circ\text{C}$ .

The ultrasonic absorption coefficient was measured by a pulse apparatus over the frequency range 5–200 MHz. In two cases, poly(*o*-bromostyrene) and poly( $\alpha$ -methylstyrene) data were also available in the frequency range 0.3–1.2 MHz from previous reverberation measurements<sup>7</sup>.

## RESULTS AND DISCUSSION

The ultrasonic spectra of the different polymer solutions are reported in Figures 1–6. As the concentration used is 5% w/v, the number of monomer units per unit volume differs from one polymer to the other. In order to compare the absorption amplitudes the vertical axis has to be shifted from the origin  $O_1$  to the origin  $O_2$ , so that the monomer unit concen-

trations are the same. The origin  $O_2$  was chosen in such a manner that it corresponded to a 5% w/v ethylbenzene solution of polystyrene, that is to say  $4.81 \times 10^{-4}$  monomer unit per ml.

In each case considered, two relaxation processes are required to fit the data in the frequency range 5–200 MHz. Thus, with the exception of poly(*p*-bromostyrene), for each relaxation process and temperature, the relaxation amplitude and frequency are given by the following functions:

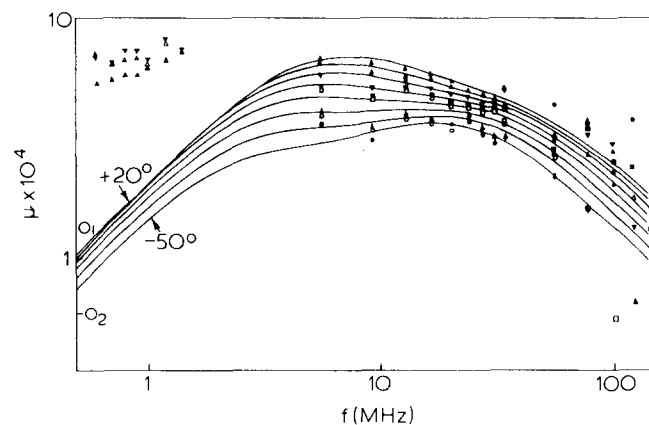


Figure 3 Ultrasonic relaxation spectra of poly(*o*-bromostyrene) in ethylbenzene. Concentration:  $5 \times 10^{-2} \text{ g cm}^{-3}$  (origin  $O_1$ );  $4.81 \times 10^{-4}$  monomer units per  $\text{cm}^3$  (origin  $O_2$ )

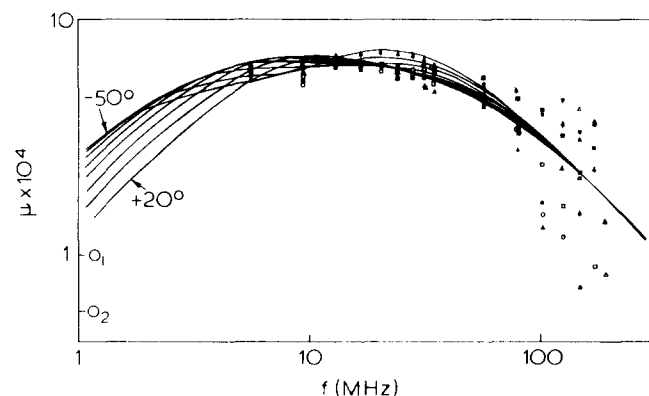


Figure 4 Ultrasonic relaxation spectra of poly(*m*-bromostyrene) in ethylbenzene. Concentration:  $5 \times 10^{-2} \text{ g cm}^{-3}$  (origin  $O_1$ );  $4.81 \times 10^{-4}$  monomer units per  $\text{cm}^3$  (origin  $O_2$ )

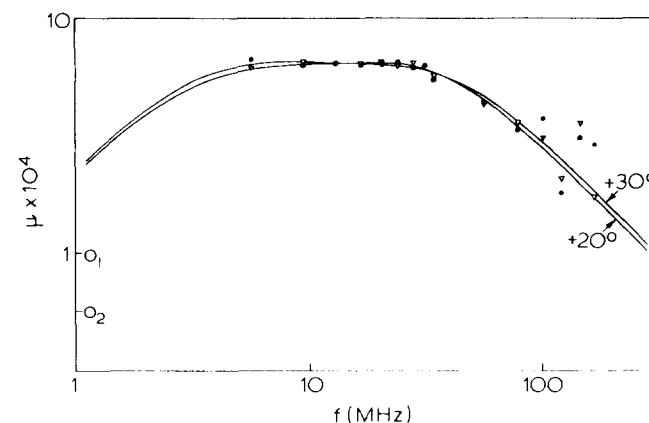


Figure 5 Ultrasonic relaxation spectra of poly(*p*-bromostyrene) in toluene. Concentration:  $5 \times 10^{-2} \text{ g cm}^{-3}$  (origin  $O_1$ );  $4.81 \times 10^{-4}$  monomer units per  $\text{cm}^3$  (origin  $O_2$ )

$$\mu_{max} = n \left( \frac{\pi RT}{2J} \right) \left( \frac{\theta_v}{C_p} \right)^2 \left( \frac{\Delta H}{RT} \right)^2 \frac{\exp(-\Delta H/RT)\exp(\Delta S/R)}{[1 + \exp(-\Delta H/RT)\exp(\Delta S/R)]^2} \quad (1)$$

$$f_c = \frac{kI}{2\pi h} \quad (2)$$

$$\exp(-\Delta H_{21}^*/RT)\exp(\Delta S_{21}^*/R)[1 + \exp(-\Delta G/RT)]$$

where  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy differences between the two states involved in the relaxation process;  $n$  is the concentration of relaxing systems and is unknown. It may be expressed as the number of monomer units required for one relaxing system; this figure must not be confused with the number of monomer units involved in the relaxation process, which number may be smaller than  $n$ .  $v$ ,  $\theta$ ,  $C_p$  are the ultrasonic velocity, expansivity and specific heat of the solution. In equation (1), the volume change associated with the rotational isomeric process has been neglected. Although this assumption is not always valid, the good agreement which has appeared between the n.m.r. and ultrasonic values of  $\Delta H$  and  $\Delta G$  in previous ultrasonic studies of 2,4,6-triphenylheptane<sup>8</sup> and polystyrene<sup>9</sup>, indicates that this assumption is allowed.  $\Delta H_{21}^*$  and  $\Delta S_{21}^*$  are the activation enthalpy and entropy between state 2 and 1.

The unknown parameters have thus been evaluated by

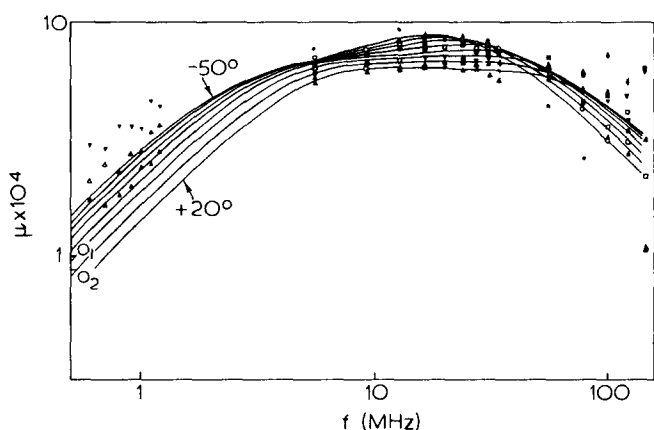


Figure 6 Ultrasonic relaxation spectra of poly( $\alpha$ -methylstyrene) in ethylbenzene. Concentration:  $5 \times 10^{-2} \text{ g cm}^{-3}$  (origin  $O_1$ );  $4.81 \cdot 10^{-4}$  monomer units per  $\text{cm}^3$  (origin  $O_2$ )

using a non-linear least squares procedure. The algorithm used<sup>10</sup> also gives the errors associated with each parameter for a 95% confidence interval. Only the data obtained by using the pulse apparatus were taken into account in the calculation and, in order to reduce the number of unknown parameters,  $n$  was given a fixed value. According to previous ultrasonic studies of polystyrene<sup>9,11</sup> this value was chosen so that there is one relaxing system for 5 or 10 monomer units depending on whether the relaxation process considered is that at high or low frequency.

In the case of poly(*p*-bromostyrene), the temperature range is not large enough for such an analysis and the ultrasonic spectra have been resolved to give two relaxation processes at each temperature:

$$\frac{\alpha}{f^2} = \frac{A_1}{1 + (f/f_{c1})^2} + \frac{A_2}{1 + (f/f_{c2})^2} + B$$

The results are given in Tables 1 and 2. For each polymer the discrepancy between the fitted curves and the experimental values slightly exceeds the error bars and, the attempt to fit the observed results with two relaxation processes is probably to be viewed as a first approximation. In fact, the absorption of poly(*o*-bromostyrene) as measured below 1 MHz is much larger than the calculated value (Figure 3). At least for this polymer, a third relaxation process arises, the characteristic frequency of which is several hundred kHz and the amplitude of which decreases as the temperature increases<sup>7</sup>. On the other hand, for poly( $\alpha$ -methylstyrene) the low frequency measurements are in rather good agreement with the fitted curves.

From Table 1 it appears at once that the thermodynamic parameters calculated for the relaxation processes of the polymers studied are very similar. It may be concluded that to a first approximation the elementary relaxation process in ethylbenzene is essentially the same in all these styrene chains so that the conformational changes postulated to account for the ultrasonic spectra of polystyrene<sup>9</sup> seem also available in the case of monosubstituted polystyrenes. The activation energies found in the present work as well as for other solvents such as decalin or MEK<sup>12</sup> are surprisingly low and sometimes negative. However, it should be noted that, taking into account the confidence interval, the possibility of positive values of  $\Delta H_{21}^*$  cannot be ruled out. Nomura *et al.*<sup>12</sup> have performed very simple conformational energy calculations on polystyrene and showed the existence of a low activation energy  $\Delta H_{21}^*$ , of only 0.8 kcal/mol for the crankshaft transition. Therefore, the observed low values of  $\Delta H_{21}^*$  mentioned in Table 1 do not seem unreasonable.

Table 1 Thermodynamic parameters of monosubstituted polystyrenes

	<i>o</i> -Me	<i>o</i> -Cl	<i>o</i> -Br	<i>m</i> -Br	$\alpha$ -Me
	Low frequency				
$\Delta H$ (kcal mol <sup>-1</sup> )	2.8 $\pm$ 0.5	3.7 $\pm$ 0.6	3.8 $\pm$ 1.3	3.3 $\pm$ 0.5	2.5 $\pm$ 1.1
$\Delta S$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	7.6 $\pm$ 0.9	10.3 $\pm$ 1.3	8.2 $\pm$ 3.0	9.2 $\pm$ 1.0	6.4 $\pm$ 1.6
$\Delta H_{21}^*$ (kcal mol <sup>-1</sup> )	1.0 $\pm$ 1.4	-1.7 $\pm$ 1.7	0.8 $\pm$ 3.1	1.4 $\pm$ 1.6	0.8 $\pm$ 3.9
$\Delta S_{21}^*$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	-20.5 $\pm$ 4.8	-17.7 $\pm$ 5.8	-21.1 $\pm$ 10.8	-18.6 $\pm$ 5.6	-21.2 $\pm$ 13.5
	High frequency				
$\Delta H$ (kcal mol <sup>-1</sup> )	1.3 $\pm$ 0.1	1.3 $\pm$ 0.1	1.9 $\pm$ 0.6	1.6 $\pm$ 0.3	1.5 $\pm$ 0.2
$\Delta S$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	5.2 $\pm$ 1.9	5.4 $\pm$ 2.3	5.9 $\pm$ 1.1	8.2 $\pm$ 3.2	5.4 $\pm$ 1.8
$\Delta H_{21}^*$ (kcal mol <sup>-1</sup> )	-0.1 $\pm$ 1.2	0.2 $\pm$ 1.4	0.2 $\pm$ 1.9	-0.4 $\pm$ 1.5	0.5 $\pm$ 1.9
$\Delta S_{21}^*$ (cal K <sup>-1</sup> mol <sup>-1</sup> )	-22.5 $\pm$ 5.6	-20.8 $\pm$ 6.5	-20.7 $\pm$ 8.2	-24.4 $\pm$ 7.4	-19.5 $\pm$ 8.8

Table 2 Relaxation amplitudes and frequencies

$T^{\circ}\text{C}$	$A_1$ $10^{-17}\text{cm}^{-1}\text{s}^2$	$f_1$ MHz	$\mu_{\text{max}}$ $10^{-4}$	$A_2$ $10^{-17}\text{cm}^{-1}\text{s}^2$	$f_2$ MHz	$\mu_{\text{max}}$ $10^{-4}$	$B$ $10^{-17}\text{cm}^{-1}\text{s}^2$
Poly( <i>o</i> -methylstyrene)							
+20	116	7.8	6.13	11.4	41.1	3.15	7.8
+10	131	6.8	6.20	13.3	38.2	3.53	7.1
0	145	5.9	6.14	15.5	35.5	3.94	6.8
-10	157	5.1	5.93	18.0	32.9	4.37	7.2
-20	167	4.4	5.59	20.8	30.4	4.80	8.1
-30	174	3.8	5.12	23.9	28.0	5.24	9.5
-40	176	3.2	4.56	27.4	25.8	5.67	11.5
-50	175	2.7	3.93	31.1	23.7	6.08	14.1
Poly( <i>o</i> -chlorostyrene)							
+20	142	8.8	8.35	9.6	46.4	2.98	7.7
+10	160	7.3	8.10	11.5	42.0	3.35	6.8
0	177	6.0	7.61	13.7	38.0	3.73	6.4
-10	190	4.9	6.93	16.4	34.1	4.14	6.6
-20	198	4.0	6.08	19.6	30.6	4.54	7.4
-30	201	3.3	5.15	23.2	27.2	4.94	8.8
-40	198	2.6	4.19	27.4	24.2	5.33	10.7
-50	189	2.1	3.27	32.2	21.3	5.68	13.3
Poly( <i>o</i> -bromostyrene)							
+20	140	6.3	5.91	8.2	40.5	2.24	6.2
+10	137	5.7	5.40	9.5	36.9	2.43	5.6
0	132	5.1	4.81	10.8	33.6	2.61	5.5
-10	124	4.6	4.17	12.3	30.5	2.76	5.9
-20	114	4.1	3.51	13.7	27.6	2.87	6.7
-30	102	3.6	2.86	15.1	25.0	2.94	8.0
-40	88.4	3.2	2.26	16.3	22.6	2.96	9.7
-50	74.9	2.8	1.72	17.4	20.4	2.92	12.0
Poly( <i>m</i> -bromostyrene)							
+20	80.4	10.1	5.46	7.5	46.4	2.33	7.1
+10	92.3	8.5	5.50	9.2	42.6	2.73	6.6
0	106	7.1	5.39	11.4	39.0	3.18	6.6
-10	117	5.9	5.13	14.1	35.5	3.68	7.0
-20	126	4.9	4.73	17.3	32.3	4.25	7.9
-30	133	4.1	4.23	21.3	29.3	4.87	9.2
-40	136	3.3	3.64	26.1	26.5	5.55	11.0
-50	135	2.7	3.03	31.7	24.0	6.26	13.2
Poly( <i>p</i> -bromostyrene)							
+20	152	4.8	4.87	23.1	29.9	4.65	4.3
+30	150	4.4	4.24	28.6	26.7	4.90	3.8
Poly( $\alpha$ -methylstyrene)							
+20	94.8	7.4	4.74	13.4	49.3	4.45	8.1
+10	106	6.6	4.83	16.2	44.0	4.95	7.6
0	116	5.8	4.83	19.5	39.0	5.45	7.6
-10	125	5.1	4.73	23.4	34.5	5.96	8.2
-20	133	4.5	4.53	28.0	30.3	6.42	9.3
-30	139	3.9	4.24	33.2	26.5	6.88	11.0
-40	141	3.4	3.86	39.3	23.0	7.30	13.3
-50	141	2.9	3.42	46.2	19.9	7.56	16.1

From Table 2, it appears that both  $f_1$  and  $f_2$  depend on the nature and position of the substituent. In fact, the ultrasonic spectra allow comparison, without any assumption, of the relaxation times and, consequently, the intramolecular mobilities of the different monosubstituted polystyrenes with each other and with that previously determined for polystyrene<sup>9</sup>. In order to minimize the molecular weight effects on ultrasonic spectra, the data presented in Figures 1-6 have to be compared with the results (Figure 7) obtained for the polystyrene sample (Pressure Chemicals Co.) of the molecular weight 200 000 ( $M_w/M_n = 1.06$ ). From this comparison, the following conclusions can be drawn:

(a) Replacement of the hydrogen atom at the *o*-position of the phenyl ring induces a shift of the ultrasonic spectra to the low frequencies. The greater the steric hindrance of the substitute, the larger the shift of the spectrum. As the

Van der Waals radius is nearly equal for the  $\text{CH}_3$  group and the Cl atom, the frequency shift is similar for poly(*o*-methylstyrene) and poly(*o*-chlorostyrene).

(b) For polybromostyrenes, the intramolecular mobility slows down with the substituent, in the order *m*-, *p*- or *o*-position, so that the intramolecular mobility appears higher in poly(*m*-bromostyrene) than in *p*- and *o*-brominated derivatives. The frequency decrease by 1.5 to 2 between the ultrasonic spectra of polystyrene and poly(*p*-bromostyrene) is in good accordance with the lowering of the relaxation frequency observed in the ultrasonic studies of the model compounds of these polymers: the 2,4-diphenylpentane<sup>13</sup> and the 2,4-di(*p*-bromophenyl) pentane<sup>14</sup>.

(c) It appears that poly( $\alpha$ -methylstyrene) behaves very much like polystyrene as previously observed by Dunbar *et al.*<sup>15</sup>. The ultrasonic spectrum of poly( $\alpha$ -methylstyrene)

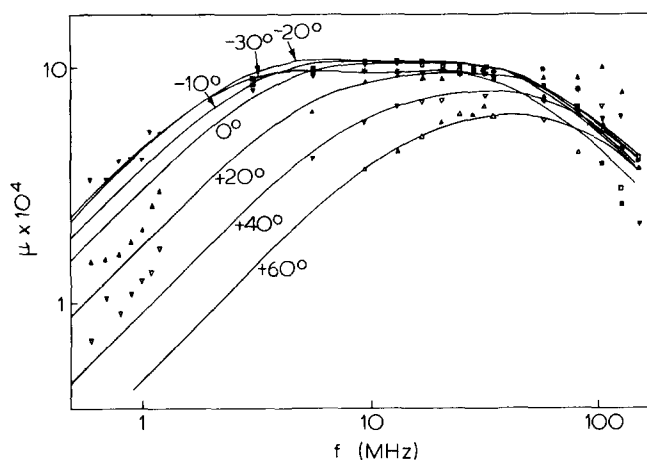


Figure 7 Ultrasonic relaxation spectra of 200 000 molecular weight polystyrene in ethylbenzene. Concentration  $5 \times 10^{-2} \text{ g cm}^{-3}$

seems only broadened on both low and high frequency sides.

These results are in good agreement with the  $^1\text{H}$  spin-echo and  $^{13}\text{C}$  spin-lattice relaxation times previously measured for these monosubstituted polystyrenes<sup>2</sup>. In particular, they corroborate the peculiar behaviour of the *m*-substituted polystyrenes, the intramolecular mobility of which seems higher. Such a result has already been observed by dielectric relaxation<sup>5,17,16</sup>. Indeed, the glass transition temperatures<sup>18</sup> of the solid polymers also suggest that the *m*-polymer chain is more flexible than the *p*-polymer. The reason is not clear but an explanation might be that the replacement of the hydrogen atom at the *m*-position of the phenyl ring by a Br atom does not affect the energy of the most stable conformations but slightly lowers the energy of the eclipsed state *tt*<sup>19</sup>. Under these circumstances the activation energy for conformational changes would be lowered and so the rate increased.

The ultrasonic data also confirm the similarity of beha-

viour of polystyrene and poly( $\alpha$ -methylstyrene). This conclusion is supported by the conformational energy calculations<sup>19</sup>. Taking into account the likely variation of the methylene bond angle, it appears that some conformational changes give the same activation energy in poly( $\alpha$ -methylstyrene) as in polystyrene.

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