Dielectric relaxation properties of poly(dimethylphenyl methacrylate)s

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The dielectric relaxations of poly(dimethylphenyl methacrylate)s were studied over a wide frequency and temperature range by two methods. The α relaxation, associated with the glass transition temperature, was studied by classical dielectric measurements. Thermal peak cleaning was used to deconvolute the global thermally stimulated current spectra over the range of low temperatures, corresponding to the β relaxation. The α relaxation involves long-range, generalized and highly cooperative motions of the main chain. They are influenced by the steric hindrance and dipole–dipole interactions relative to the position of the CH_3 group of the aryl ring in the polymer repeat unit. As a first approximation it was assumed that the β process was related only to local motions of the side group, but the activation parameters are too high to be consistent with this assumption. Therefore it was concluded that intermolecular factors and local motions of the main chain could also be involved.

(Keywords: dielectric relaxation; PDMPs; thermally stimulated currents)

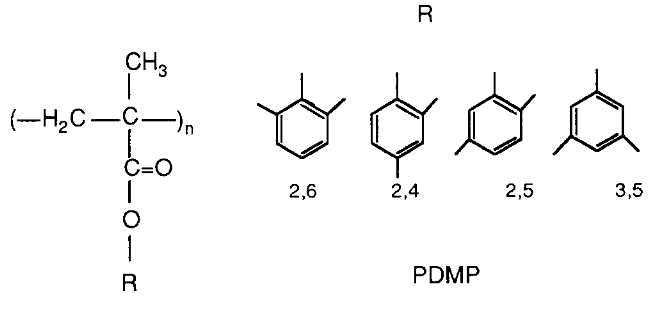
INTRODUCTION

Whereas it is well recognized that the most prominent relaxation in amorphous polymers, the glass–rubber or α relaxation, is caused by long-range, generalized and cooperative motions of the main chain[1], the exact nature of the secondary relaxations taking place at temperatures below the glass transition temperature, where long-range motions are frozen, is not yet well understood[2].

As it is assumed that the subglass relaxation or β process is related to reorientation of flexible side groups in polymer chains, it was considered interesting to investigate a group of synthetic dimethyl-substituted polymers such as the poly(dimethylphenyl methacrylate)s (poly[1-(dimethylphenyloxycarbonyl)-1-methylethylene]s) with 2,4, 2,5, 2,6 and 3,5 disubstitution (see *Scheme 1*). In this way it should be possible to obtain a better understanding of the molecular origin of the relaxation process and to estimate the influence of the steric hindrance and dipole–dipole interactions relative to the positions of the two methyl groups which both lie in a single plane for 120° or 180° of the aryl ring.

To improve this study, we chose two experimental methods i.e. thermally stimulated current (t.s.c.) measurements and conventional alternating current (a.c.) dielectric techniques, which, when used together, cover a wide frequency range[3].

The disadvantage of classical a.c. dielectric techniques is that the relatively high probe frequencies (1 MHz) cause the various transitions due to molecular motions to merge together at higher frequencies. But the measured dielectric parameters are very useful for studying the α-relaxation process. The t.s.c. technique is highly sensitive and gives reproducible results in terms of polymer transitions. The low equivalent t.s.c. frequency ($\sim 10^{-4}$ to 10^{-2} Hz) leads to enhanced resolution of the different relaxation processes, especially the β-relaxation process. A thermal peak cleaning of the t.s.c. global spectra is often used to study broad relaxation peaks as the low temperature secondary relaxation peaks.



Scheme 1 Substitution patterns of the PDMPs

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EXPERIMENTAL

Monomer and polymer preparation

2,4-Dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl and 3,5-dimethylphenyl methacrylates were obtained by reaction of methacryloyl chloride (50% solution in benzene) with the corresponding phenol in the presence of triethylamine as acid acceptor, following the experimental procedure previously reported[4–6]. Polymers were obtained by radical polymerization in benzene solutions under vacuum using AIBN as initiator[4–6]. These polymers have predominantly syndiotactic triads (mm 0.26, mr 0.48 and rr 0.26) similar to those reported for poly(methacrylate)s prepared under the same conditions[7,8], including poly(methacrylic acid)[9].

The samples studied correspond to fractions of similar molecular weights with narrow molecular weight distributions (see *Table 1*).

Preparation of the samples

Samples for dielectric measurements were obtained by moulding under a hot press. They were then put in a heater at 60°C under vacuum in order to remove humidity.

For dielectric measurements, discs of 20–25 mm diameter and 1 mm thickness were used. For t.s.c. measurements, plates of approximately 50 mm^2 and 1 mm thickness with silver, metallized faces were used.

Measurements

A dielectric analyser DEA 2970 from TA Instruments coupled to a 2100 thermal analyser was used to measure the dielectric parameters of the samples. The a.c. dielectric experiments were done by using the parallel plate sensors. The DEA module provided real-time quantitative calculations of the dielectric parameters for 12 frequencies in the range 0.3 to 10^5 Hz from -150 to 250°C at a heating rate of 1°C min^{-1}. Internally, it converted the measured sample response (capacitance C, conductance $1/R$ and phase angle shift δ) into permittivity and loss factor using

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

$$\varepsilon'' = \frac{d}{RA2\pi f \varepsilon_0} \qquad (1)$$

where d is the sample thickness, ε_0 is the permittivity of vacuum (8.854×10^{-12} F m^{-1}), A is the metallized electrode area, f is the frequency of the experiment and R is the resistance of the sample.

A t.s.c. spectrometer (Solomat Instruments) was used over the temperature range -150 to 160°C. A Faraday cage shielded the samples. The sample cell was previously evacuated to $\sim 10^{-4}$ mbar and subsequently flushed several times with 1100 mbar of high purity He. Two different methods of polarizing the sample were used to obtain 'global' t.s.c. spectra or thermally cleaned t.s.c. spectra.

Table 1 Number average molecular weights, weight average molecular weights and polydispersity indices for 2,6-PDMP, 2,4-PDMP, 2,5-PDMP and 3,5-PDMP

Polymer	$10^{-5}M_n$	$10^{-5}M_w$	M_w/M_n
2,6-PDMP	1.95	2.34	1.20
2,4-PDMP	1.98	2.09	1.10
2,5-PDMP	1.25	1.56	1.25
3,5-PDMP	1.21	1.46	1.20

Method 1. For global spectra the film was first polarized by a static electric field ($E = 500$ V mm^{-1}) at the polarization temperature T_p for 2 min, and then quenched down to the freezing temperature. With the field turned off and the sample short circuited the depolarization current due to dipolar reorientation was measured as the temperature was increased from T_0 at 7°C min^{-1} to the final temperature T_f ($\geqslant T_p$).

Method 2. Thermal cleaning was performed by applying the polarization field ($E \approx 500$ V mm^{-1}) during the following thermal cycles: 2 min at T_p, quenching to $T_p - 10$°C (window of 10°C), and holding for 2 min more. The field was then removed and the sample was quenched down to a temperature $T_0 = T_p - 40$ at approximately 20°C min^{-1}. The depolarization spectra due to a narrow distribution of relaxations were then measured upon heating at 7°C min^{-1} to temperatures about 30°C above T_p.

The global t.s.c. is a convoluted spectrum of all dielectrically active relaxations excited between T_p and T_0. The method used to analyse the thermally cleaned t.s.c. spectrum was integration. The relaxation time $\tau(T)$ is related to the measured depolarization current iT) by

$$\tau(T) = \frac{P(T)}{i(T)} = \frac{\int_{T_0}^{T} i(T)d}{i(T)t} \qquad (2)$$

where T_0 is the initial temperature of the depolarization scan. It is assumed that the relaxation time constant τ is related to the barrier height or apparent activation energy E_a in the Arrhenius equation

$$\tau(T) = \tau_0 \exp(E_a/RT) \qquad (3)$$

where τ_0 is the pre-exponential factor. The values of $\ln \tau(T)$ are plotted against reciprocal temperature. A linear dependence of $\ln \tau$ *versus* $1/T$ is found with the slope equal to E_a.

The second method of analysing the thermally cleaned spectrum uses the Eyring equation

$$f = \frac{kT}{2\pi h} \exp(-\Delta H^{\neq}/RT) \exp(\Delta S^{\neq}/RT) \qquad (4)$$

where k is Boltzmann's constant, h is Planck's constant and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the Eyring activated states of enthalpy and entropy, respectively. In this way the values of the thermodynamic parameters are calculated.

RESULTS AND DISCUSSION

Global spectra

The imaginary part of the dielectric constant ε'' at 1 kHz is plotted against T in *Figure 1*, and *Figure 2* shows the global t.s.c. multiplot for the four polymers studied. The t.s.c. depolarization current is analogous to a conventional dielectric loss signal with an equivalent frequency of the order of 10^{-3} Hz. Therefore, the shape of each spectrum is similar, except for the very high temperature peaks in t.s.c. thermograms which do not appear in dielectric a.c. spectra. They are due to free charges and are called ρ peaks.

The low temperature zone corresponds to the β relaxation; the absorption is weak and it is extended over a large span of temperatures. The β process is suggested to be associated with the motions of the entire side-chain groups[10–12].

The spectra show prominent absorptions at high temperatures with high and sharp peaks attributed to the glass–rubber transition. The last peaks in the t.s.c. spectra correspond to the conductivity of the material; they are present at very high temperatures and are called ρ peaks.

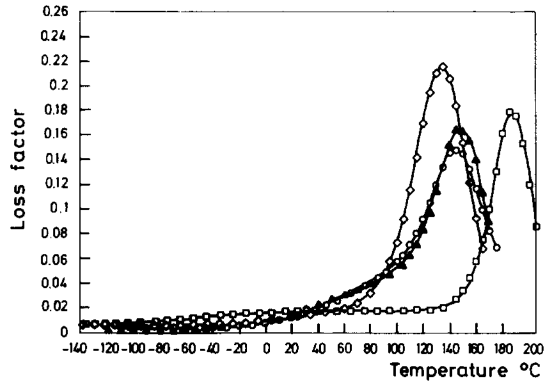

Figure 1 Dielectric loss factor at 1 kHz: (□) 2,6-PDMP; (○) 3,5-PDMP; (◇) 2,5-PDMP; (▲) 2,4-PDMP

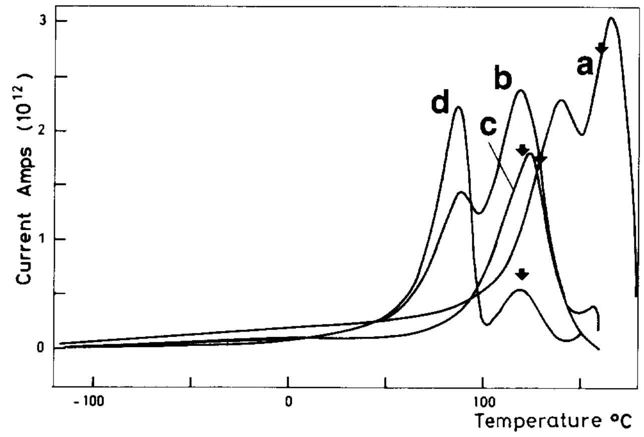

Figure 2 Full t.s.c. spectra for the four polymers studied: (a) 2,6-PDMP, 167°C; (b) 2,4-PDMP, 109°C; (c) 3,5-PDMP, 106°C; (d) 2,5-PDMP, 111°C

In discussing the α temperatures of the group of polymers[11], it should be mentioned that 2,6 substitution (i.e. in both available *ortho* positions) leads to very high steric hindrance. The 2,6-PDMP α-temperature zone is detected higher by about 50°C when compared with the other polymers of this group. Differences of only 3 or 4°C in the temperature zone are observed among 2,4-PDMP, 3,5-PDMP and 2,5-PDMP. The main characteristic of 2,5-PDMP is that the dipoles introduced with the methyl substituents cancel each other because they diverge in direction bt 180°; consequently, interaction with the COO group dipole is absent.

Since the α zone of this polymer lies at the lower temperatures, it seems that the lack of dipole–dipole interaction makes easier the segmented mobility. Concerning the β relaxation, 3,5-PDMP presents the most important absorption and 2,5-PDMP seems to have the weakest process in the glass system.

After these observations we studied each process separately. The α relaxation was studied using the measured dielectric parameters, while the secondary relaxation was studied using the thermal peak cleaning of the β zone of temperatures.

The α-relaxation process

Complex dielectric plane plots for our four polymers are shown in *Figure 3*. The experimental arc was obtained by shifting the isothermal curves of ε' and ε'' in frequency by application of the time–temperature superposition principle, effecting a horizontal and eventually a vertical shift of each one. This is made possible by the relaxed and unrelaxed permittivities (ε_0 and ε_∞) being nearly temperature independent. In all cases, the α absorption is represented by skewed arcs which approach the abscissa in the high frequency region through a straight line. Curves are fitted by the Havriliak–Negami empirical equation[13]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1+(jw\tau_0)^{1-\alpha}]^\beta} \qquad (5)$$

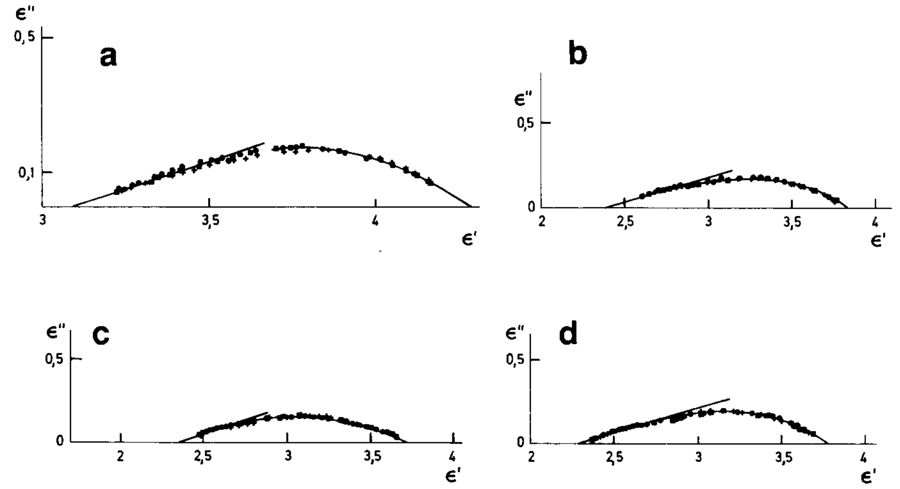

Figure 3 Cole–Cole plots for the polymers studied: (+) experimental data; (■) Havriliak–Negami model; (●) biparabolic model. Reference temperatures: (a) 2,6-PDMP, 167°C; (b) 2,4-PDMP, 109°C; (c) 3,5-PDMP, 106°C; (d) 2,5-PDMP, 111°C

where ε_0 and ε_∞ are the relaxed and unrelaxed dielectric constants in the process, j is $\sqrt{-1}$, τ_0 is the umbral relaxation time, w is the angular frequency, $1-\alpha$ is the width parameter and β represents the skewing in the α process, and by the biparabolic equation[14–17]

$$\varepsilon^*(w)=\frac{\varepsilon_0\varepsilon_\infty[1+\delta(jw\tau)^{-k}+(jw\tau)^{-h}]}{\varepsilon_0-\varepsilon_\infty+\varepsilon_\infty[1+\delta(jw\tau)^{-k}+(jw\tau)^{-h}]} \tag{6}$$

The mechanical counterpart of this equation comes from a theory of the non-elastic deformations developed from a molecular mobility model. The parameters δ, h and k have precise physical meanings, taking into account the effectiveness of correlation effects exhibited during the molecular motions involved in the process. Values of ε_0, ε_∞ and the parameters of the two models are given in *Tables 2* and *3*.

From the comparison of the three arcs (see *Figure 3*), the biparabolic equation fits the experimental data better than the Havriliak–Negami equation, even though the two models give good results. The polymer 2,6-PDMP has the weakest intensity ($\varepsilon_0-\varepsilon_\infty$), meaning that its process of α relaxation involves fewer dipoles than the others. This is consistent with the fact that the glass transition lies at a higher temperature. The molecular chains must pass through high potential barriers, so they have many difficulties to overcome in reorienting their dipoles. 2,5-PDMP has the highest value of $\varepsilon_0-\varepsilon_\infty$ and the smallest α zone of temperatures.

Obviously, in the limit of low and high frequencies the parameters of the two models determine the frequency dependence of the dielectric loss in the α relaxation[18,19]. Therefore, they are related by a mathematical equation: at very high frequencies ($w\to\infty$) $k=\beta(1-\alpha)$, and at very low frequencies ($w\to 0$) $k=(1-\alpha)$. *Table 4* shows that these relationships are quite well verified.

The k and $\beta(1-\alpha)$ values depend on the polymer behaviour in the range of high frequencies for the α relaxation, i.e. inducing the easiest and fastest cooperative motions. On the other hand, h and $1-\alpha$ depend on slower movements (higher temperatures, lower frequencies). Therefore, the quantitative values of these parameters give information about these motions in proportion to the global α process.

Table 2 Values of ε_∞, ε_0 and the parameters given by one of the models applied to the polymers studied

Polymer	ε_∞	ε_0	$\varepsilon_0-\varepsilon_\infty$	α	β
2,6-PDMP	3.093	4.259	1.166	0.4683	0.3713
2,5-PDMP	2.280	3.760	1.480	0.5280	0.4140
2,4-PDMP	2.390	3.835	1.445	0.5867	0.4720
3,5-PDMP	2.380	3.712	1.332	0.6896	0.8510

Table 3 Values of the parameters given by one of the models applied to the polymers studied

Polymer	h	k	δ
2,6-PDMP	0.4950	0.1950	0.650
2,5-PDMP	0.4967	0.1850	0.212
2,4-PDMP	0.4278	0.1972	0.988
3,5-PDMP	0.3214	0.2621	1.650

Table 4 Values of the parameters given by the two models in the limits of low and high frequencies for the polymers studied

Polymer	$\beta(1-\alpha)$	k	$1-\alpha$	h
2,6-PDMP	0.1972	0.1950	0.5311	0.4900
2,5-PDMP	0.1954	0.1850	0.4720	0.4967
2,4-PDMP	0.1951	0.1972	0.4133	0.4278
3,5-PDMP	0.2641	0.2621	0.3104	0.3214

Table 5 Values of T_g, T_∞, the free volume at the glass transition temperature, and the expansion coefficient of the free volume at T_g for the polymers studied

Polymer	T_g (°C)	T_∞ (°C)	ϕ_g	$\alpha_f\times10^3$ (K^{-1})	$\rho^{2\,a}$
2,6-PDMP	167	115	0.0596	1.146	0.9987
2,5-PDMP	111	60	0.0416	0.816	0.9951
2,4-PDMP	109	59	0.0309	0.618	0.9930
3,5-PDMP	106	51	0.0509	0.925	0.9910

[a] Correlation coefficient

Free volume theory[20]

The α processes in the polymers studied are assigned to the cooperative motions around T_g. Because of these motions the α processes can follow a William–Landel–Ferry (WLF) behaviour for the shift factor α_T of the isothermal curves of ε''. The equation followed is

$$\log\alpha_T=\frac{-C_1(T-T_g)}{C_2+T-T_g}=\frac{m}{T-T_\infty}+B \tag{7}$$

where $T_\infty=T_g-C_2$ and $C_2\approx 50$°C.

The slope m of each straight line is related to the relative free volume ϕ by

$$m=\frac{B}{\phi}(T-T_\infty)=\frac{B}{\phi_g}(T_g-T_\infty) \tag{8}$$

where B is assumed to be unity and ϕ_g is the free volume at the glass transition temperature. On the other hand, the expansion coefficient of the free volume at T_g is given by

$$\alpha_f=\frac{\phi_g/B}{T_g-T_\infty} \tag{9}$$

Values of T_g, T_∞, ϕ_g and α_f are given in *Table 5*.

The values for ϕ_g are slightly different from the predicted theoretical value (0.0252 ± 0.005). 2,6-PDMP is the polymer which has the highest value of ϕ_g, and this value decreases with temperature owing to reduced molecular motions. Since the chains of 2,6-PDMP are the slowest, the volume set at the glass transition temperature should be the highest. The value found for 2,5-PDMP seems to be quite high, especially when we compare it with the 3,5-PDMP value. Indeed, the chains of the former are faster and the free volume of the latter is larger as a result of the two substitutions at positions 3 and 5. The trustworthiness of these values is in doubt.

The α-relaxation process is attributed to the micro-Brownian motions of the main chain, involving long-range, cooperative motions. We can interpret these cooperative motions as a succession of correlated movements in the whole structure which depends on the configuration that the chains take at each instant and on the available volume.

The main-chain mobility depends slightly on the ease of lateral group motion, so the respective positions of the methyl groups influence this mobility because of their important steric volume[11].

Stronger steric hindrance results from *ortho* substitution: the phenyl groups seem to be highly restricted in rotation, and therefore the structure becomes inflexible and the chains cannot change configuration easily. This is the case for 2,6-PDMP with the methyl groups in both available *ortho* positions. The position of the end of the lateral group involves another problem. Owing to the repulsive forces from crowding of the methyl groups on the ring and the methyl group on the polymer backbone the segmental motion may be limited. It appears that a possible contribution resulting from dipole–dipole interaction is very weak.

The β-relaxation process

The β zone extends over a large temperature range. This is a characteristic of the secondary process which involves local motions of the lateral groups[3]. They are more diversified movements with a large spectrum of relaxation times. Therefore, thermal cleaning of the t.s.c. global spectra (or windowing polarization) is used to study the broad relaxation peaks of the low temperature secondary relaxation. This is effective because it allows one to excite only the specific transition of interest[3].

Figure 4a shows the thermally cleaned spectrum for 2,6-PDMP as an example. Each peak corresponds to a window of polarization of 10°C and to an extremely narrow relaxation time distribution.

The plot of $\ln \tau$ against $1/T$ resulting from each peak integration allows one to determine the activation parameters of the process. Values of these parameters are shown in *Tables 6* and *7* for the polymers studied.

E_a is related to $\Delta H^{\neq}$ by $E_a = \Delta H^{\neq} + RT$. The value of RT is of the order of $0.5\,\mathrm{kcal\,mol^{-1}}$ at normal temperatures and is only a small contribution. That is why the values of E_a and $\Delta H^{\neq}$ are so close. These two parameters represent the energy barrier that the chains must pass through during their movements. The values seem to be adequate for secondary relaxations but perhaps too high for only local and independent motions of the local groups[21].

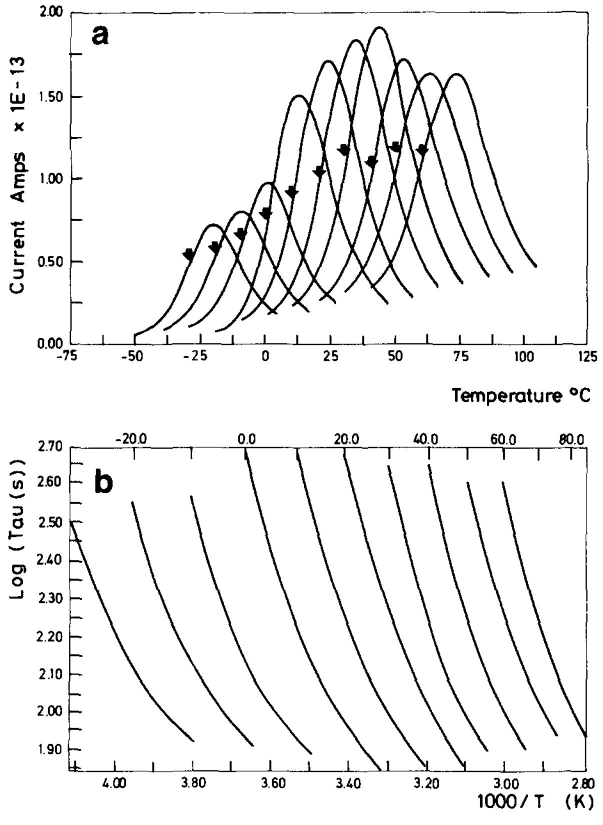

Figure 4 (a) Partial depolarization (see *Tables 5* and *6* and Experimental for details) and (b) relaxation map analysis for 2,6-PDMP

Table 6 Arrhenius parameters for the polymers studied at the polarization temperature T_p and the temperature at the maximum of each peak T_m

Polymer	T_p (°C)	T_m (°C)	$\log \tau$	E_a (kcal mol^{-1})
2,6-PDMP	−30.0	−20.5	−5.052	8.69
	−20.0	−9.6	−5.398	9.48
	−10.0	0.8	−5.605	10.13
	0.0	12.6	−5.976	11.11
	10.0	14.0	−6.222	11.88
	20.0	34.4	−6.341	12.46
	30.0	43.4	−6.868	13.61
	40.0	53.1	−6.821	13.99
	50.0	62.7	−6.472	13.85
	60.0	73.1	−6.859	14.90
2,4-PDMP	−40.0	−29.0	−6.084	9.48
	−30.0	−19.7	−6.532	10.39
	−20.0	−9.5	−6.532	10.82
	−10.0	0.6	−7.661	12.67
	0.0	11.8	−7.772	13.37
	10.0	23.3	−7.234	13.18
	20.0	33.6	−9.056	16.20
3,5-PDMP	−40.0	−26.4	−6.645	10.25
	−30.0	−17.2	−6.634	10.66
	−20.0	−6.3	−7.017	11.59
	−10.0	2.9	−6.578	11.42
	10.0	23.6	−6.573	12.34
	20.0	33.5	−6.916	13.27
2,5-PDMP	−40.0	−27.8	−7.142	10.73
	−30.0	−19.9	−8.600	12.74
	−20.0	−9.8	−7.236	11.66
	−10.0	0.1	−8.133	13.25
	0.0	9.7	−7.818	13.30
	10.0	20.8	−8.605	14.95

The activation entropy corresponds to the density fluctuations of the material during the relaxation process. It is quite constant but with negative values[22].

The initial hypothesis was that the β-relaxation process of the PDMP involved local and independent motions of the side chains, taking into account the broadness of the spectra and the distributions of the values for the activation parameters. It seems that the movements are much more complicated and that intermolecular and intramolecular motions occur. A change in conformation or a lateral rotation does not occur without a correlated motion of that part of the main chain close to the side group or without a change of conformation of a neighbouring lateral group. These intermolecular hindrances to reorientation contribute to the energy barriers and lengthen the relaxation time. The two methyl groups have an influence on the flexibility of the lateral groups and on the free volume of the glassy structure.

In the case of 3,5 substitution, the excluded volume from the rotation of the disubstituted phenyl is large, leading to an increased free volume. The local motion thus becomes easier in the glassy state. On the contrary, the 2,5 substitution, for which the net effect of the steric hindrance, the overall bulkiness of the substituents and the absence of dipole–dipole interaction result in a higher segmental mobility, has not an important available

Table 7 Thermodynamic parameters

Polymer	T_p (°C)	T_m (°C)	ΔH (kcal mol^{-1})	ΔS (cal deg^{-1} mol^{-1})	ΔG (kcal mol^{-1})
2,6-PDMP	−30.0	−20.5	7.8545	−37.0033	16.8463
	−20.0	−9.6	8.5041	−35.5008	17.5858
	−10.0	0.8	9.1987	−34.6278	18.3059
	0.0	12.6	10.1249	−33.0353	19.1435
	10.0	24.0	10.8413	−31.9776	19.8910
	20.0	34.4	11.3825	−31.5165	20.6168
	30.0	43.4	12.4747	−29.1250	21.2998
	40.0	53.1	12.8066	−29.4276	22.0175
	50.0	62.7	12.6668	−31.0938	22.7101
	50.0	73.1	13.6452	−29.3783	23.4282
2,4-PDMP	−40.0	−29.0	8.6521	−32.2871	18.1750
	−30.0	−19.7	9.5056	−30.2150	16.8479
	−20.0	−9.5	9.9120	−30.2856	17.5743
	−10.0	0.6	11.6532	−25.1976	18.2801
	0.0	11.8	12.3045	−24.7909	19.0724
	10.0	23.3	12.0812	−27.3532	19.8221
	20.0	33.6	14.9727	−19.0848	20.5646
3,5-PDMP	−40.0	−26.4	9.3836	−29.6625	16.2949
	−30.0	−17.2	9.7383	−29.8055	16.9810
	−20.0	−6.3	10.6185	−28.1440	17.7391
	−10.0	2.9	10.4520	−30.2201	18.3998
	10.0	23.6	11.2616	−30.4200	19.8706
	20.0	33.5	12.1385	−28.9303	20.6151
2,5-PDMP	−40.0	−27.8	9.8439	−27.4097	16.2303
	−30.0	−19.9	11.7423	−20.8484	18.8079
	−20.0	−9.8	10.7118	−27.0967	17.5672
	−10.0	0.1	12.2191	−24.5973	18.9446
	0.0	9.7	12.2295	−24.5973	18.9446
	10.0	20.8	13.8095	−21.0038	19.7536

free volume in the glassy structure. The first local movements cannot begin easily at low temperature and the β relaxation is nonexistent.

The secondary process depends on the broadness of the motions and the non-equilibrium state of the polymer during the polarization. Indeed 2,6-PDMP, whose molecules are the slowest, presents a weak β process. The relaxation involves few dipoles with small motions. Moreover, the chains are closer to their equilibrium state than the chains of the other polymers and the energy barrier is lower because the activation parameters are lower.

The molecular mechanism of this secondary relaxation is not well understood but the important source is thought to be reorientation associated with flexible side groups[2,18,19]. We can affirm that the movements involved at low temperatures are local but depend on the variation of the packing in the glass about individual reorienting groups. In conclusion, there is a cooperativity in the movements and the correlation increases with temperature[21].

CONCLUSIONS

T.s.c. and dielectric techniques were used to study molecular relaxations in poly(dimethylphenyl methacrylate)s, allowing us to verify the general hypotheses concerning the processes involved in these polymers.

The observations of the global spectra were related to the differences between the four polymer substitutions. The methyl groups, with their large steric volume, hinder cooperative motions of the entire chains by restricting the phenyl group rotation.

For the glass transition or α relaxation, a WLF type of deviation from simple Arrhenius behaviour was found in the dielectric results. The Havriliak–Negami and biparabolic models were found to fit well with the experimental dielectric data.

Thermal peak cleaning of the t.s.c. global spectra led to activation parameters from Arrhenius and Eyring equations. The values obtained as a function of the polarization temperature T_p increased and were quite high for energy barriers resulting from intramolecular effects alone.

It was assumed that the β process is related to local and independent flexible side group motions in polymer chains. But the results showed that this relaxation seems to be produced by motions of the side groups presumably coupled with motions of a few skeletal bonds of the main chain, and that intermolecular interactions play an important role in the development of these motions.

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