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Donor-acceptor interaction effects on dielectric relaxation of methacrylic polymers

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A series of methacrylic copolymers with various densities of donor-acceptor interactions was analyzed by means of Dielectric Relaxation Spectroscopy. Two dielectric relaxations, one in the temperature region of the glass-rubber transition, and the other in the glassy state, were observed. The influence of donor-acceptor interactions on the first relaxation was especially investigated. From the analysis of frequency dependent data, the Vogel temperature, the fraction of free volume and the relaxation time at the glass transition temperature were determined for each copolymer composition by assuming that the VFTH plots must be straight lines in the non-Arrhenius region starting from the glass transition temperature. A procedure to diminish the conductivity effects in temperature swept dielectric spectra is proposed.

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Keywords: Donor-acceptor copolymers, Donor-acceptor interactions, Relaxation time, Glass transition

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1. Introduction

Among other interesting properties, the polymers with electron donor (D) and electron acceptor (A) side groups on the same backbone are photoconductive materials with potential applications in different light sensitive devices. Syntheses and studies of chemical structure for polymers with such groups bonded on acrylic and methacrylic chains were first performed by Simionescu, Percec and Natansohn [1] as early as the beginning of the years ’80. Investigations of their properties in solid state as photoconductivity [2, 3], thermal and mechanical behavior [4, 5] as well as magnetic resonance relaxation [6], were carried out some years later, but studies about the dielectric relaxation spectroscopy (DRS) have not been reported up to now.

An interesting characteristic of such copolymers is that the glass transition temperature, T_g, shows a positive deviation from the weighted average of the homopolymers, with maximum for the equimolar composition. A major goal of the present study was to obtain information about the dielectric relaxation time at the glass transition temperature, τ_g. This is not a simple objective because even the very long ago known and utilized phenomenon of glass transition in polymers is not yet satisfactorily explained up to now. So, there are still numerous aspects to be clarified for this process [7] what does to tell about it as a mysterious phenomenon [8] without adequate theories and models [9]. The following fact is clear: the molecular motion does not cease but continues under the so-named glass transition temperature, T_g, what determines unwanted dependences of the experimental values on the measuring conditions for any kind of measurement used up to now. The temperature where the cooperative motion of a macromolecular chain completely stops is defined as that where the equilibrium conformational entropy becomes zero, and it is known as the Kauzmann temperature in calorimetric studies and as the Vogel temperature in dielectric measurements. The last temperature appears as T_0 in the old but still much used VFTH (Vogel-Fulcher-Tammann-Hesse) equation (1) [10-12], which is an empirical relationship between the dielectric α-relaxation time, τ, and the temperature T, with m as a material dependent constant.

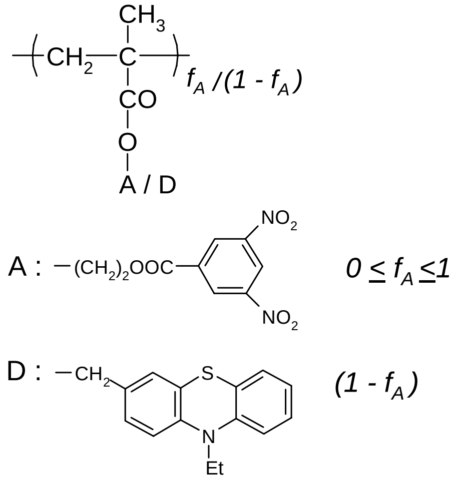
$$\ln \tau / \tau_0 = m / (T - T_0) \quad \text{(VFTH eq.)(1)}$$

Although, theoretically, the VFTH equation performs best for polymers which show small deviations from Arrhenius behavior, particularly for $T > T_g + 50$ K [7], it has been found that it applies even near T_g if the temperature T_0 is adequately chosen [13]. In fact, if the origin of the temperature scale is T_0 instead of 0 K, the VFT equation resembles the more general Arrhenius relationship, which is a quasi-empirical equation describing the temperature dependence of the activation energy in numerous physical and chemical processes. The insoluble problem is that the Vogel temperature T_0 as well as the Kauzmann temperature can not be directly measured. An approximate relationship, $T_0 = 0.77\ T_g$, was established from calorimetric [14] and viscosimetric [15] measurements and even proved for a series of amorphous polymers [13]. Although there is a theoretical foundation for this relationship, there are pertinent observations which contradict a universal T_0/T_g ratio. Starting from this fact, the values of T_0 for the series of polymers presented in this article were determined by using the hypothesis that the VFT plots are straight lines in the non-Arrhenius region starting from around T_g, what means that the temperature dependence of the α-relaxation time is an exponential function of $1/(T - T_0)$.

2. Experimental

2.1 Basic characterization of polymers

Scheme 1 presents the chemical structures of the studied polymers. They contain D and A groups of phenothiazinyl and 3,5-dinitrobenzoyl types, respectively. The series of these polymers contains copolymers with various ratios between the concentrations of the two groups as well as the corresponding homopolymers. The polymers were obtained as reported [16] and their characteristics of interest for the present study are given in Table 1.



Scheme 1. Chemical structure of studied polymers.

Table 1. Compositions and glass transition temperatures for the copolymers.

Sample	P1	P2	P3	P4	P5	P6	P7	P8	P9
f_A	0	0.11	0.22	0.35	0.47	0.62	0.75	0.87	1
T_g (K)	376.9	384.3	388.8	390.7	390.5	388.7	385.4	380.9	376.0

f_A - the molar fraction of A units in the copolimer (^{1}HNMR determinated).

The chain microstructure was established from 400 MHz ^{1}HNMR spectra recorded at room temperature from $CDCl_3$ solutions using an Avance DRX 400 MHz Bruker NMR spectrometer. The values T_g were taken from the literature [17] and are determined from DSC thermograms recorded on second heating with 10 K/min using a Pyris Diamond DSC set-up from Perkin Elmer.

2.2 Dielectric measurements

Measurements of the dielectric response in the frequency range from 1 to 10^6 Hz and temperatures comprised between -100 and +170 ^{0}C were carried out using a Novocontrol Concept 40 broadband dielectric spectrometer. The temperature in the cryostat was controlled with 0.1 ^{0}C stability by a Novocontrol Quatro Cryosystem in a dry nitrogen atmosphere.

For dielectric analysis each sample was prepared and measured as follows. First, a pellet of pressed polymer powder was heated during pressing up to 170 ^{0}C between two circular stainless steel electrodes of 20 mm diameter. Three small strips of Kapton (DuPont product) with 125 μm thickness were used as spacers; the surface of the spacers has about 5% of the electrode aria, so that the dielectric data of the studied polymers are not much influenced.

The prepared samples were measured first at seven fixed frequencies, 1, 10^1, 10^2, 10^3, 10^4, 10^5 and 10^6 Hz, by sweeping the temperature from -100 to +170 ^{0}C with 5 ^{0}C/min heating rate, and second, by sweeping the frequency between 1 and 10^6 Hz at fixed temperatures, at 4 ^{0}C intervals, for the temperature above T_g, corresponding to α process.

The results from frequency scan were analyzed using the Novocontrol software WinFit. Each relaxation peak was described by fitting with a function composed from an exponential term for the conductivity effect and a Havriliak-Negami (HN) term [18] for α relaxation:

$$\varepsilon(\omega) = \varepsilon' - i\varepsilon'' = -i(\sigma_0 / \varepsilon_0 \omega)^n + \{\varepsilon_u + (\varepsilon_r - \varepsilon_u)/[1 + (i\omega\tau_{HN})^a]^b\} \tag{2}$$

$$\tau = \tau_{HN}\{\sin[\pi ab/(2+2b)]/\sin[\pi a/(2+2b)]\}^{1/a} \tag{3}$$

where σ_0 is the d.c. conductivity, n is an exponential factor, ε_0 is the permittivity of free space, $\Delta\varepsilon=\varepsilon_r$ - ε_u represents the intensity of relaxation, where ε_r and ε_u represent the relaxed ($\omega\rightarrow 0$) and unrelaxed ($\omega\rightarrow\infty$) values of the dielectric constant for each relaxation, $\omega=2\pi f$ is the angular frequency, a and b represents the symmetric and asymmetric broadening parameters, τ_{NH} is the so-named HN relaxation time, and τ is the actual relaxation time for the considered process [19].

Thus the position of the maximum of dielectric loss was extracted and the activation plots for α relaxation, log τ vs. temperature, were realized.

3. Results and discussion

3.1 Dielectric isochronous measurements and comparison of α relaxation and glass transition

The temperature dependence of loss tangent, tan *δ*, at 10^4 Hz for all the polymers in the series is represented in Figure 1. A weak relaxation peak appears at negative temperatures which, as for other polymethacrylates, has been appointed as β relaxation and attributed to the rotation of side groups [20-22]. One can observe that the temperature corresponding to this peak, T_β, increases slightly when the acceptor fraction, f_A, increases up to 0.5 and then decreases. This dependence supports the supposition that the lateral group mobility decreases with the density of DA interactions. Another observation would be the fact that the β relaxation is lighter for the homopolymer P1 ($T_\beta \cong$ -50 ºC at 10^4 Hz) than for the homopolymer P9 ($T_\beta \cong$ -20 ºC at 10^4 Hz), what would be explained by the side chain length that is shorter for P1 than for P9, the side chain masses being practically equal, 284 and 283 Da.

Unlike the other samples in the series, the samples P3-P5 show wide and without maxim β relaxation peaks. The observed plateau might be the superposition of two relaxations, what would suggest that the movements of the two types of lateral groups are somehow independent.

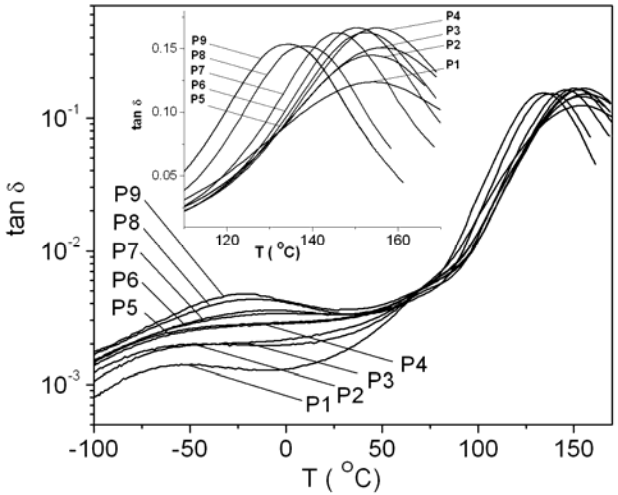


Fig. 1. Temperature dependence of loss tangent at 10^4 Hz in -100 to +165 ^{0}C temperature domain; inset are represented the spectra in α relaxation temperature region.

On the other hand, each polymer in the series exhibits a single α relaxation temperature, T_α, which is above T_g and growing with the electric field frequency. The dependence of the peak position, T_α, on f_A is similar with that of the temperature T_β, so that a shift to higher temperatures when f_A increases if $f_A < 0.5$ and a reversal shift when $f_A > 0.5$. When the electric field frequency and the fraction f_A decrease, T_α approaches T_g, but the α relaxation becomes less and less observable due to the overlapping of the electric conductivity effect which amplifies at the same time (fig. 2). At frequencies of 1 Hz or lower, the α relaxation signal of the most samples appeared as a wide shoulder, without any maximum, and, consequently, without the possibility to read directly the temperature T_α. At somehow higher frequencies the α peak is visible but its position is apparently located at a temperature higher than real one because of the summation of dipolar and conductive losses, being known that conductivity increases exponentially with temperature.

In order to separate the dipolar contribution, a calculation procedure where an exponential conductivity signal, *σ(T),* was subtracted from the tan *δ(T)* signal in the temperature region of α relaxation was developed. Such a method is somehow similar with the before presented Havriliak-Negami method which is destined to the processing of frequency swept dielectric spectra. So, an Arrhenius type function 4 was chosen for the temperature dependence of conductivity, and its parameters *E* and σ_0 were determined with equation 5 and 6 using the coordinates of two points (T_1, y_1) and (T_2, y_2), situated on each side of the α relaxation peak. The ordinate *y* is just *tan δ*.

$$\sigma(T) = \sigma_0 \exp(E_a / T^{1/4}) \tag{4}$$

$$E = \frac{T_1 T_2}{T_1 - T_2} \ln \frac{y_2}{y_1} \tag{5}$$

$$\sigma_0 = y_1 \left(\frac{y_2}{y_1} \right)^{T_2/(T_2 - T_1)} \tag{6}$$

This procedure is illustrated in Figure 2 for two samples, one of high content of D groups and the other of high content of A groups. The looseness of this procedure may arise from the choice of the two limit temperatures which must be completely apart from the α relaxation peak. The values of T_α at low frequencies obtained by the spectra processing illustrated in Fig. 2 are compared in Table 2 with the values found from unprocessed spectra. One can observe that the error caused by the conductivity is more pronounced as both the fraction f_A and the frequency decrease.

Table 2. T_α values in absolute degrees at several low frequencies as resulted for the copolymer samples P2 and P8 by direct reading (DR) and signal processing (SP).

f (Hz)	P2		P8	
	DR	SP	DR	SP
10^0	-	384.4	374.1	372.8
10^1	398.3	393.2	380.7	379.2
10^2	405	403.3	388	388
10^3	416.1	414.5	397.7	397.7

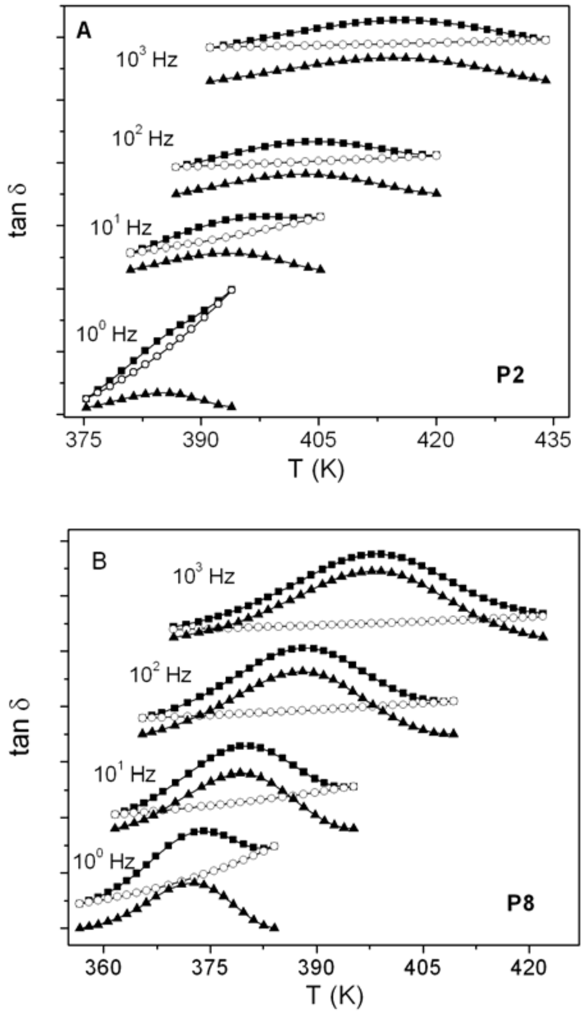


Fig. 2. Separation of the dipolar components (triangle symbols) by subtracting the conductivity components (empty circles) from the isochronous tan δ spectra (squares) of low frequencies from P2 (A) and P8 (B) copolymers.

Equation 7, where $T_{\alpha D}$ and $T_{\alpha A}$ are the α relaxation temperatures of the two homopolymers, P1 and P9, at a certain frequency, would be the Fox equation, commonly used to determine the glass transition temperature in systems with non-interacting components (polymer blends and statistical copolymers) [23], transposed here to predict the relaxation temperature T_α at the chosen frequency for the copolymers studied, P2 to P8.

$$\frac{1}{T_\alpha} = \frac{f_A}{T_{\alpha A}} + \frac{1-f_A}{T_{\alpha D}} \tag{7}$$

However, as illustrated for 10^4 Hz in Fig. 3, the equation 7 does not explain the dependence of the temperature T_α on the polymer composition even at sufficiently high frequencies where the conductivity contribution is negligible (see Figures 1 and 2), what means that the Fox model is not applicable. On the other hand, this fact confirms the presence of the interactions between the donor and acceptor groups which are most probably responsible for the positive deviation of the temperature T_α from a Fox like composition dependence. As in the case of the glass transition temperature, T_g, (Table 1), the deviation is maximum for f_A equals approximately 0.5, where the density of DA pairs is expected to be maxim [24].

As before mentioned, the composition dependence of the temperature T_g was previously reported for our copolymers from DSC measurements [17], and the present dielectric relaxation findings are to the same effect.

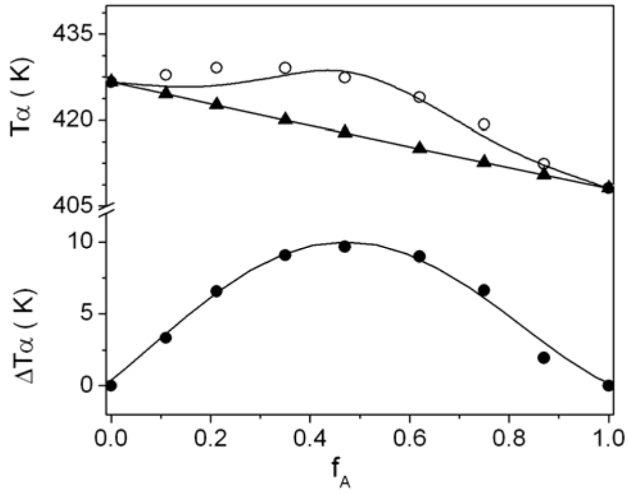


*Fig. 3. T_α (K) at 10^4 Hz vs. f_A; experimental (**o**) and calculated with the Fox equation 7 (▲) values. Below, the difference between the two values is plotted. The solid line curve passing through the experimental values T_α corresponds to equation 7 with $c = 3.1$ M, $K_a = 1.3\ M^{-1}$ [27] and $K = 3.5\ K{\cdot}M^{-1}$.*

In another attempt to explain the dependence T_α (f_A), the hypothesis of a similitude between the effects of the DA interactions and those of the crosslinks on the glass transition temperature is used. The crosslinking effects are described by the Fox-Loshaek equation [25]. So, starting from the equation we gave in a previous article [26] for the dependence T_g (f_A), the following equation can be written for the dependence in discussion at a certain frequency:

$$T_\alpha = T_{\alpha 0} + K \cdot c \cdot f_A(1-f_A)[1+f_A(1-f_A)-1/(K_a \cdot c)]/\{1-c \cdot f_A(1-f_A)[1+f_A(1-f_A)-1/(K_a \cdot c)]\} \tag{8}$$

where K_a is the constant of DA association, K would be an empiric constant, c is the total concentration of D and A groups, assumed to be the same for all copolymers, indifferently of the copolymer composition given by the molar fraction f_A, and $T_{\alpha 0}$ is the α relaxation temperature at the chosen frequency in the absence of DA interactions.

The temperature $T_{\alpha 0}$ may be given by equation 7, namely $T_{\alpha 0} = T_{\alpha A}\, T_{\alpha D}/[f_A\, T_{\alpha D} + (1 - f_A)\, T_{\alpha A}]$, or by the weighted arithmetic mean for the two homopolymers, namely $T_{\alpha 0} = f_A\, T_{\alpha A} + (1 - f_A)\, T_{\alpha D}$. The maximum of T_α at $f_A = 0.5$ results observing that T_α increases continuously with the product $f_A\ (1 - f_A)$ and that this product is maxim for $f_A = 0.5$. The plot of equation 8 in Fig. 3 was obtained using $c = 3.1$ M, $K_a = 1.3$ M^{-1} [27] and $K = 3.5$ K degree·M^{-1}, the last value being obtained for a best fitting with the experimental points. To calculate the value T_α for other frequency it is necessary to change adequately the value of $T_{\alpha 0}$. The difficulty with the predictability with equation 8 is that the values $T_{\alpha D}$ can be obtained with an acceptable error only for frequencies higher than about 10^3 Hz.

3.2 α relaxation from isothermal dielectric measurements

Dielectric loss spectra $\varepsilon''(f)$ at temperatures above T_g are represented in Fig. 4A for the sample P4. As a normal characteristic for the α relaxation is the shift to higher frequencies with increasing temperature. At lower temperatures the α peak is much overlapped by conductivity losses. Conduction increases with increasing temperature but at higher temperatures the relaxation signal is better separated. One observes in Figure 4B, where the dielectric spectra at 148 ^{0}C are presented for all the samples that the conductivity distortions are most pronounced for the samples P1 and P2, so that when the amount of donor groups is high.

As mentioned in Experimental section, the relaxation time values were determined by means of the HN equation completed with an exponential term that accounts the conductivity contribution, which is especially outstanding at low frequencies and for predominantly donor samples. It was observed that the Arrhenius plots, log τ vs. inverse temperature, are not straight lines but show curvatures more and more pronounced as the temperature approaches T_g. As mentioned before, the VFTH equation 1 [10-12], where τ_0 is the relaxation time at infinite temperature, is commonly used to correlate the α relaxation rate with the sample temperature. Based on the observation that the dependence log τ vs. $1/(T - T_0)$ is linear for many amorphous polymers and copolymers even when $T \rightarrow T_g$ [13], we determined the values of the Vogel temperature, T_0, and of the parameter m for each sample, therefore the dependences $T_0(f_A)$ and $m(f_A)$, by assuming the linearity of the VFTH dependence over the non-Arrhenius region from more than $T_g + 50$ K up to T_g surrounding.

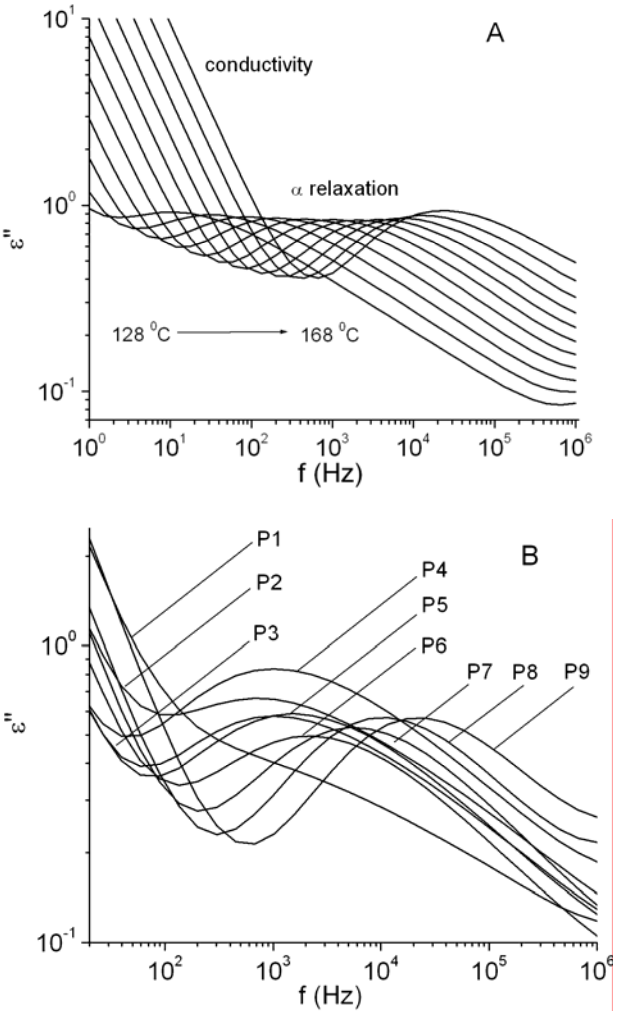


Fig. 4. ε''(f) spectra of the sample P4 for various temperatures in the α relaxation range (A) and the spectra ε''(f) for all the polymers at 148 ^{0}C (B).

The resulting curves obtained for the best-fit are represented in Fig. 5 and the corresponding VFT parameters are summarized in Table 2. Also there are included in Table 2 the fraction of free volume at T_g, namely the ratio Φ_g/B of relationship 9, where B is a parameter close to unity related to the ratio between the critical volume for a relaxation process to take place and the volume of the segments intervening in the process [28], as well as the values of the α relaxation time at T_g, τ_g, resulted from the equations of the straight lines in Fig. 5 for $T = T_g$.

$$\frac{\Phi_g}{B} = \frac{T_g - T_0}{m} \qquad (9)$$

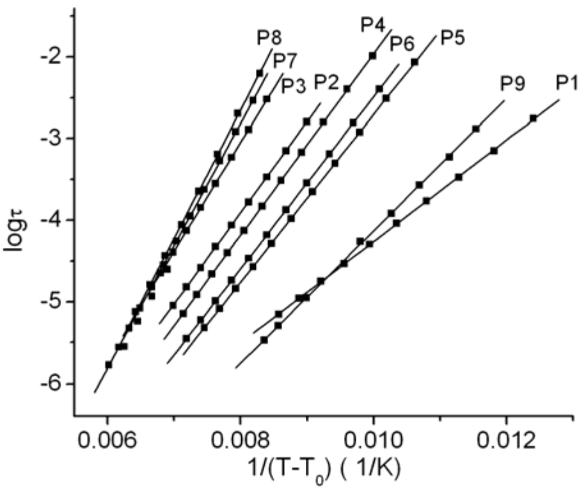


Fig. 5. VFT plots, log τ vs. 1/(T-T_0), where T_0 was determined for the linearization of VFT representation.

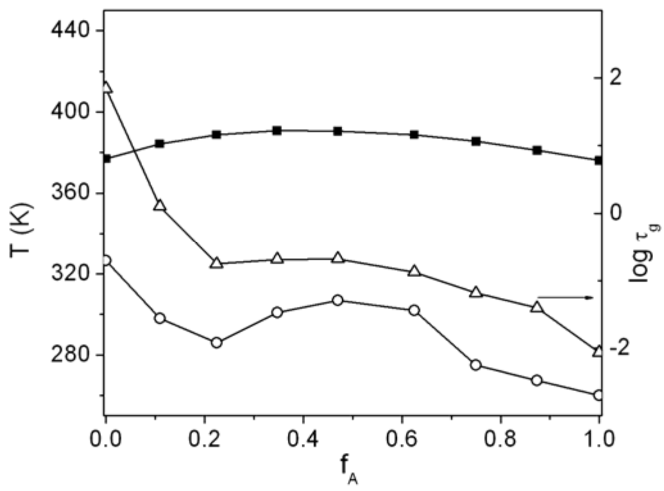


Fig. 6. Plots of composition dependences: DSC determinate T_g (■) and T_0 values obtained as mentioned in the text (o) (left axis), and log τ_g (Δ) (right axis).

Table 2. VFT parameters obtained for eq.(9), the fraction of free volume at glass transition, ϕ_g /B, and the extrapolated relaxation time at glass transition temperature, τ_g.

Sample	T_0 (K)	log τ_0	m (K)	ϕ_g /B	τ_g (s)
P1	326.5	-10.5	621.7	0.134	6.32
P2	298	-12.9	1117.9	0.225	1.11
P3	286	-13.7	1326.9	0.264	0.47
P4	301	-13.1	1110.3	0.230	0.50
P5	307	-13.0	1027.6	0.214	0.51
P6	302	-13.0	1053.8	0.223	0.42
P7	275	-14.8	1499.6	0.286	0.30
P8	267.5	-15.2	1573.7	0.298	0.25
P9	260	-14.7	1465.9	0.309	0.13

One observes that, for about the equimolar composition, the Vogel temperature, T_0, shows a relative maximum, therefore is not a material constant as it has been formerly considered [15] , (Table 2 and Figure 6), while the fraction of free volume at T_g, ϕ_g /B, seems to be minimum (Table 2). The maximum of the relaxation time at T_g, τ_g, is not so clear due to the conductivity effects which much increases when the fraction f_A tends to zero, so that for predominantly donor polymers.

4. Conclusions

Two types of dielectric relaxations, α and β, are observable for the series of polymers between – 100 and + 170 ^{0}C. The two relaxation peaks shift to higher frequencies or temperatures when the fraction f_A increases up to 0.5, and then the dependences are inverted.

The conductivity effects in spectra, which intensify when the donor character increases, was attenuated by using the HN procedure for isothermal spectra and a proposed method for isochronal spectra.

An explanation based on a similitude between DA interactions and crosslinks is proposed for the maxima of the temperatures T_α observed at about the equimolar composition of polymers.

Values of some relaxation parameters as the Vogel temperature, the α relaxation time at T_g and the fraction of free volume at T_g are determined under the assumption that the VFTH relationship is linear from high temperatures up to T_g surrounding.

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