SOME CHARACTERISTICS SPECIFIC TO COPOLYMERS CONTAINING DONOR AND ACCEPTOR SIDE GROUPS

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Donor-acceptor copolymers with phenothiazine and dinitrobenzoate side groups were studied with the aim to complete and explain the characteristics of such polymers. So, NMR determination of association constant, effects of the donor-acceptor interactions in IR absorption spectra as well as the absence of a visible influence of the mentioned interactions on the polymer microstructure are presented and discussed. It was observed that the composition dependence of the glass transition temperature does not correlate with those of the molecular mass and size. An equation based on complexation kinetics and assuming similar effects of donor-acceptor interactions and crosslinks is developed and matched with the dependence before mentioned.

INTRODUCTION

The polymeric charge transfer complexes are polymers with electron donor (D) and electron acceptor (A) groups hung up or inserted into the main chain. The present study refers to the first type of polymers where, due to some degree of motion freedom, the two types of side groups can intramolecularly associate between them by so-named donor-acceptor (DA) or charge transfer (CT) interactions. Copolymers with phenothiazine and 3,5-dinitrobenzoate side groups as D and A groups, respectively, distant by relatively long spacers to the methacrylic main chain are presented (Scheme 1).

The first syntheses of such polymers were reported by Inami *et al.*[1] but a wide variety of chemical structures were created by Simionescu, Percec and Natansohn.[2,3] In spite of some special properties as photoconductivity[4] and photorefrac-timetry,[5] these interacting polymers are still expected to be turned to applications of non-linear optics, liquid crystalline supramolecular organization as well as polymer blend compatibilization and so far. Such a situation is partially caused by both an insufficient knowledge of the specific DA interactions and non-reliable or even absent measurements of utilization properties. It is the goal of this paper to improve the knowledge about the interactions in these polymers.

Characteristics reported up to now for donor-acceptor copolymers, others than those before mentioned, would be: (i) positive deviations from the weighted averages of the corresponding homopolymers, with maxima at about the equimolar composition, for the glass transition temperature, T_g,[6] and the mass density,[3] (ii) some composition dependent effects in proton,[2] and carbon-13 [6a] NMR spectra, and (iii) CT absorptions in visible range which are wide and without observable maxima.[2,7] The present article refers to the first two characteristics, exhibiting measurements, explanations and theoretical treatments. There are also presented for the first time DA interaction effects observed in IR absorption spectra. The association constant was determined for polymer solutions, therefore it is related to intramolecular interactions, while other aspects are for bulk samples, where the DA interactions may be both intra and intermolecular. All of these are original contributions which allow a better understanding of the processes, what it is expected to lead to grounded applications.

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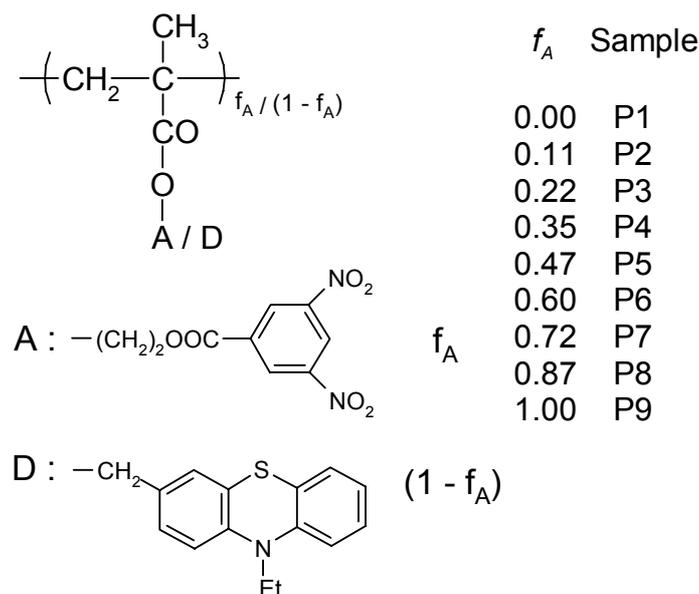
Scheme 1 – Chemical structure and encoding of studied polymers.

RESULTS AND DISCUSSION

Determination of the DA association constant, K_a

The NMR signal of the chemically equivalent 3,5-dinitrobenzoate (A group) protons H_2 and H_6, which is as a matter of fact the only signal in the spectrum well separated from the others, was used. Its pattern and position are presented in Fig. 1 for polymers containing A groups. There being an only signal for the uncomplexed and complexed states, the position of which being dependent on the composition, means that the dinitrobenzoate groups change rapidly relative to the NMR time scale between the two states.

The complexation of the groups A and D

$$D \quad + \quad A \quad \underset{k_-}{\overset{k_+}{\rightleftarrows}} \quad DA \ (ctc)$$
$$([D]_0 - x) \quad ([A]_0 - x) \quad k_- \quad x \qquad (1)$$
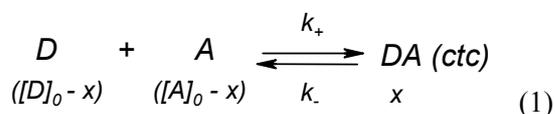
is an equilibrium reaction and, using its rate equation at equilibrium (2) and the dependence of the NMR chemical shifts on the concentration of the species in the sample solutions, the association constant defined by equation (3) can be calculated with equation (4), where x is the concentration of DA associated pairs at the equilibrium, $c = [A]_0 + [D]_0$ is the total initial concentration of A and D groups, n is the ratio between the numbers of copartners per complex, and $r = \Delta\delta / \Delta\delta_{CTC}$ is the ratio of chemical shifts differences $\Delta\delta = \delta_0 - \delta(f_A)$ and $\Delta\delta_{DA} = \delta_0 - \delta_{DA}$, the three chemical shifts, δ_0, δ_{DA} and $\delta(f_A)$, being those for the uncomplexed and complexed states, and for the sample of f_A composition, respectively. The expression (4) is valid for the so-named NMR single-point method.[8,9] This is a variant of the Benesi-Hildebrand equation,[10] which is applied in the case when the system presents an only NMR signal for the two states, complexed and uncomplexed.

$$k_+ \ ([A]_0 - x) \ ([D]_0 - x) = k_- \ x \qquad (2)$$

$$K_a = k_+/k_- = [DA]/([D] \ [A]) \qquad (3)$$

$$K_a = r \ / \ [c \ f_A \ (1 - r) \ (1/f_A - 1 - n \ r)] \qquad (4)$$

The fact that the complex is of 1:1 type is supported by the position at about $f_A = 0.5$ of the maximum of the product $f_A \cdot \Delta\delta$ (Fig. 2). So, the values of K_a in Table 1 were calculated by using equation (4) with $n = 1$. The apparent dependence of K_a on f_A is most probably caused by the measuring errors for the chemical shifts. By averaging, results $K_a = 1.3 \pm 0.3$ M^{-1}. A value $c = 3.1$ M was used for the all polymers, indifferently on the composition, because the two comonomers have practically equal molar masses, $M_A = 324$ Da and $M_D = 325$ Da. An approximate density of 1 g/cm^3 was also considered for all samples.
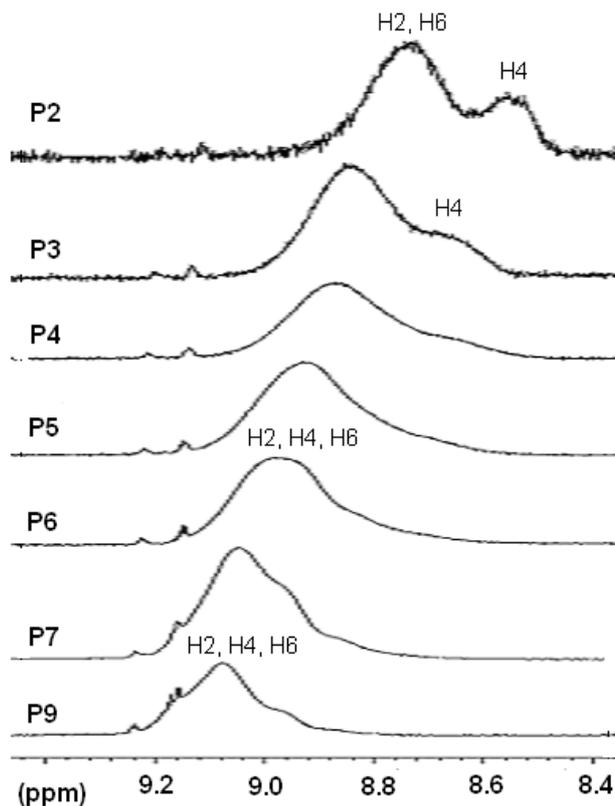
Fig. 1 – NMR signal for the protons H_2, H_4 and H_6 of 3,5-dinitrobenzoate groups in analyzed polymers.
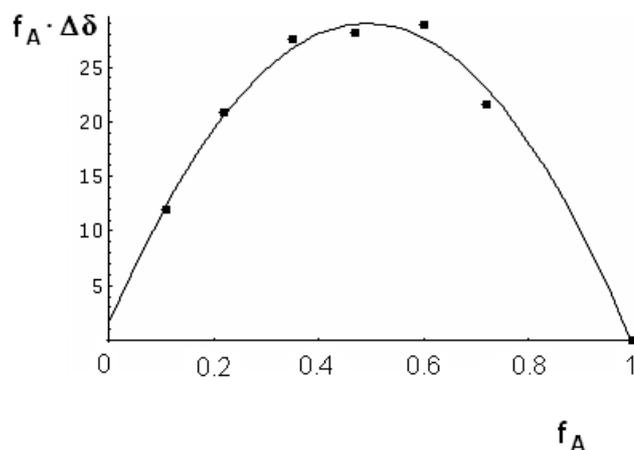

Fig. 2 – Plot of the product $f_A \cdot \Delta\delta$ in Table 1 to establish the type of DA complex.

Table 1

Data from measurements and processing of H2 and H6 NMR signal to find K_a according to equation (4).
Chemical shifts are given in Hz and referred to $CHCl_3$ signal

Sample	P9	P7	P6	P5	P4	P3	P2	DA complex
f_A	1.0	0.72	0.60	0.47	0.35	0.22	0.11	
δ (Hz)	712 (δ_0)	682	664	652	633	625	615	δ_{DA} = 590.5
$\Delta\delta$ (Hz)	0	30	48	60	79	87	97	$\Delta\delta_{DA}$ = 122
$f_A \cdot \Delta\delta$	0	21.6	28.8	28.2	27.6	19.1	10.7	0
$r = \Delta\delta / \Delta\delta_{DA}$	0	0.246	0.393	0.492	0.647	0.715	0.793	
K_a (M^{-1})		1.06	1.28	1.15	1.21	1.34	1.59	

Polymer chain microstructure

Fig. 3 shows the proton NMR signal of the methyl group directly bonded on the main chain for the homopolymers P1 and P9 as well as for three copolymers of different compositions. As observed, the polymer composition does not change significantly either the signal splitting in three components or the relative intensities of the components. Moreover, such a splitting aspect is specific to any common methacrylate polymer, like poly(methyl methacrylate) for example, and is attributed to the three tacticity triads: syndiotactic (S), heterotactic (H) and isotactic (I).[1] The fact that the signal S is the strongest for all samples indicates that the backbone configuration is mainly determined by the reciprocal steric hindrance of the methyl groups, and not by the DA interactions. These interactions would have led to a predominantly isotactic configuration, but the signal I is negligible in all cases.

Moreover, it was found by means of proton NMR spectra that the composition of the copolymers is nearly the same with that of the corresponding polymerization medium for all samples. This means that the DA interactions between the two comonomers do not affect significantly the sequence distribution on the growing macromolecular chain.

The both observations before presented confirm the rather small value determined in the previous section for the association constant, K_a.

Evidences in IR spectra for DA interactions

Unlike the observations in the previous sections, which refer to liquid solutions, the IR absorption spectra were obtained from films of solid polymers where the DA interactions would be denser because the solvent is absent. Nevertheless, the spectra of the copolymers seem to be simple weighted sums of the homopolymer spectra. However, the difference spectrum in Fig. 4 shows some additional absorptions which might be attributed to DA associations, as follows: (i) A weak absorption at about 2256 cm^{-1} is present only in the copolymer spectra. It moves from 2253 to 2258 cm^{-1} when the concentration of A groups increases. Such absorption is unusual and may arise from nitro groups with separated charges, which would be a limit form promoted by the interactions with phenothiazine (donor) groups. (ii) A new absorption of medium intensity at 910 cm^{-1} is also a characteristic only for the copolymers. Its origin might be the acceptor homopolymer absorption band at 922 cm^{-1} (nitro C-N deformation) that intensifies and is bathochromically shifted for DA states. (iii) A third characteristic of DA complex state is a strong intensification of the very weak deformation band at 649 cm^{-1} that belongs also to the acceptor structural units.
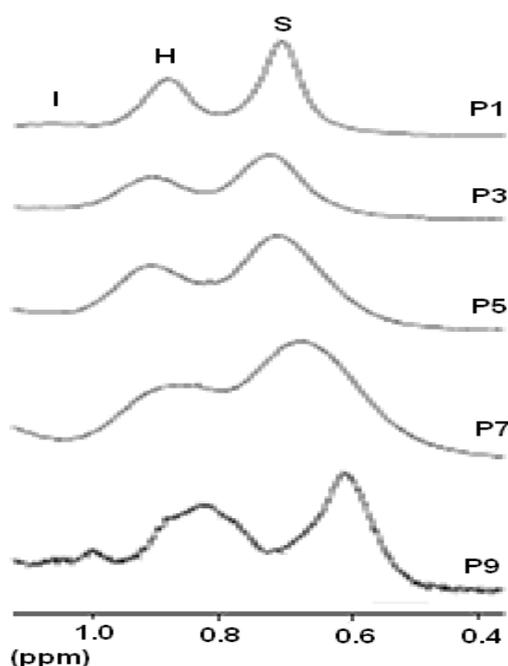

Fig. 3 – Tacticity splitting of the methyl ^{1}H-NMR signal for several samples.
The notations I, H and S are for isotactic, heterotactic and syndiotactic triads.
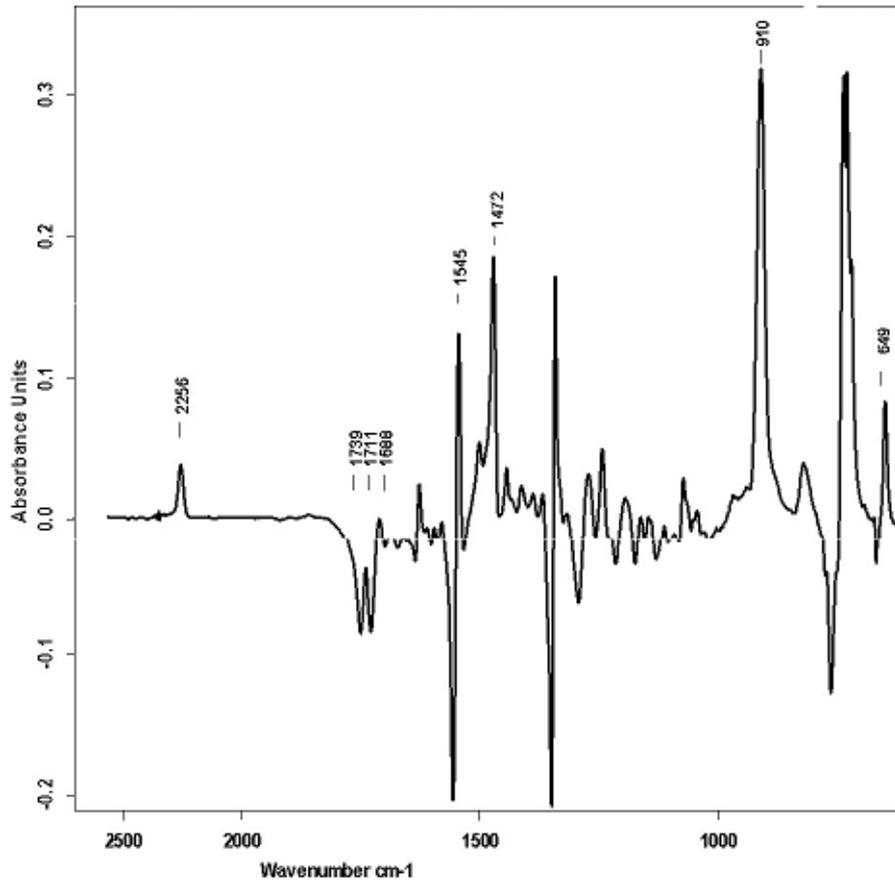
Fig. 4 – Difference FTIR spectrum between the spectrum of the copolymer P5 (equimolar composition) and the spectrum sum of the two homopolymers P1 and P9. The scaling of the sum terms was so that the difference absorptions at 1472 cm^{-1} (multiplet, C-H deformation of various alkyl groups) and 1545 cm^{-1} (singlet, C-C stretching in nitro aryl groups) to cancel as better as possible.

Composition dependence of glass transition temperature. Experimental dependences

Fig. 5 shows how the glass transition temperature, T_g,[12] and the parameters of molecular mass and size, M_w and R_g, change with the molar fraction of A units, f_A. One observes that the dependence $T_g(f_A)$ does not correlate either with the dependence $M_w(f_A)$, which shows a minimum, or with the dependence $R_g(f_A)$, that is rapidly growing. So, an explanation for the dependence $T_g(f_A)$ must be looked for elsewhere. The next section contains an explanation based on DA interactions.
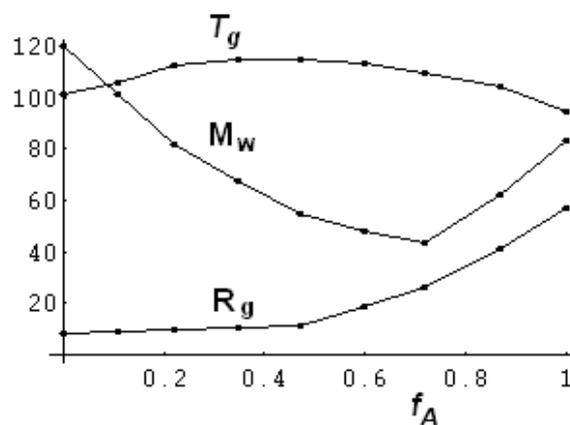

Fig. 5 – Experimental plots of T_g in ^{0}C, M_w in kDa and R_g in nanometers, all versus f_A.

Modeling the composition dependence of T_g in donor-acceptor copolymers

Such dependences have been also measured for several DA copolymer systems,[6] including that described in this paper.[12] The main feature is a weak maximum observed at about the equimolar composition, namely when $[D]_0 \cong [A]_0$ if the sum $[D]_0 + [A]_0$ is the same for the all polymers. Till now, such a characteristic has been considered as an inherent reality. A treatment based on the kinetics of DA interactions and considering that these interactions influence the temperature T_g in a similar mode as the crosslinks is presented further on.

A first step is to find the expression of the concentration of DA pairs assuming that the sum concentration $c = [D]_0 + [A]_0$ is a constant for the whole series of polymers. So, solving equation (2), the following expression results for the normalized concentration of DA associations at equilibrium, $x_e = [DA]/c$,

$$x_e = 0.5\ (1 + 1/K_a\ c) -$$
$$- 0.5\ [(1 + 1/K_a\ c)^2 - 4 f_A\ (1 - f_A)]^{0.5} \qquad (5)$$

It was found that the solution with positive radical term is useless because x_e would be often greater than unit.

Now, to find the composition dependence of the glass transition temperature, T_g, under the hypothesis that the DA interactions act similarly with the crosslinks, the Fox-Loshaek equation[13]

$$T_g = T_{g\infty} + K_c\ X_c\ /\ (1 - X_c) \qquad (6)$$

where $T_{g\infty}$ is the maximum glass transition temperature of the linear polymer, K_c is an empiric constant and X_c is the crosslinking density, can be used, by replacing X_c with x_e. It is to be mentioned that the crosslinking density is defined as the fraction of crosslinked units, so that it is a normalized concentration as x_e. The expression (7) is for the T_g as a function of the molar fraction f_A, where the function $x_e(c, K_a, f_A)$ has got the expression (5). The temperature $T_{g\infty}$ in the Fox-Loshaek equation, which is valid for homopolymers, is replaced with $T_{gA}\ f_A + T_{gD}\ (1 - f_A)$, which would be the weighted glass transition temperature for a blend of two homopolymers that would not interact one with the other.

$$T_g = T_{gA}\ f_A + T_{gD}\ (1 - f_A) +$$
$$+ K\ x_e(c, K_a, f_A)/(1 - x_e(c, K_a, f_A)) \qquad (7)$$

The maximum of T_g at $f_A = 0.5$ can be found by means of the first derivative or simpler as follows: one easily finds that T_g increases continuously with x_e, and x_e increases continuously with the product $f_A\ (1 - f_A)$ and this product is maxim for $f_A = 0.5$. Graphical illustrations of equation (7) are presented in Fig. 6. One observes that the curve 1 with $K_a = 1.3$ M⁻¹ (NMR determined value in CDCl₃) matches with the experimental points better than the curve 2. The maxim height can be easily modified with the parameter K, which takes rather high values.
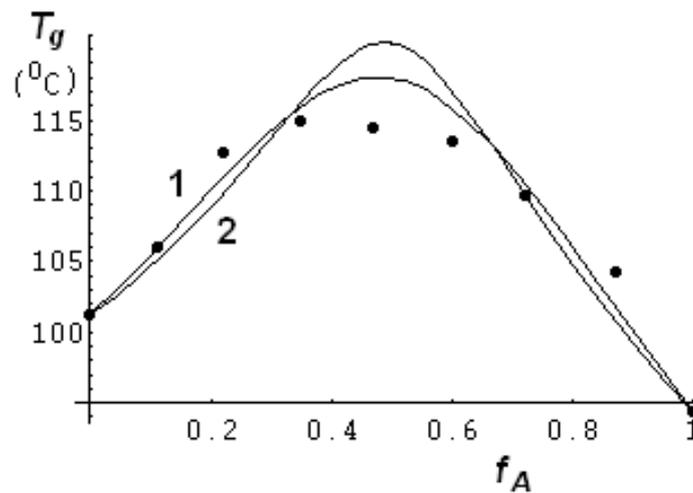

Fig. 6 – Plots of T_g versus f_A: experimental values (●) and modeling curves obtained with equation (7) for $K_a = 1.3$ M⁻¹ and $K = 60$ (curve 1) and for $K_a = 6$ M⁻¹ and $K = 40$ (curve 2).

EXPERIMENTAL

The polymers were obtained in the laboratory by using a procedure which, together some polymer characteristics, is described elsewhere.[7] The thermal behavior is characterized by DSC determined T_g values which were also taken from the literature.[12]

Table 2

Samples and characteristics used

Sample	f_A	M_w (kDa)	R_g (nm)	T_g (^{0}C)
P1	0.0	120.0	8.1	101.2
P2	0.11	100.7	8.8	106
P3	0.22	81.4	9.5	112.7
P4	0.35	67.4	10.3	115
P5	0.47	54.5	11.1	114.4
P6	0.60	48.1	19.1	113.5
P7	0.72	43.1	26.0	109.7
P8	0.87	62.4	40.9	104.3
P9	1. 0	83.4	57.1	94.3

Table 2 contains some data for the polymers implied in this study. The composition is expressed by the molar fraction of A units, f_A. and the values of the weight average mass, M_w, and of the radius of gyration, R_g, arise from Multiangle Light Scattering measurements performed in THF by means of a DAWN DSP MALS photometer provided with 633 nm HeNe laser and completed with Optillab rEX differential refractometer, the both being Wyatt products. The ^{1}H-NMR spectra were recorded at 400 MHz and 30 ^{0}C on rather diluted solutions by using CDCl$_3$ as the solvent and TMS reference signal. Alternatively, the signal from traces of CHCl$_3$ was used as reference for the aromatic proton signals. A Bruker Avance DRX 400 NMR spectrometer was used. The IR absorption spectra were obtained from polymer films casted on KBr tablets and recorded with a Bruker FTIR Vortex-70 spectrophotometer. The IR spectra were processed with a Bruker-Optics OPUS 6.5 software.

CONCLUSIONS

The distance of 6-8 bonds between the interacting groups and the backbone is sufficiently long to assure side chain flexibility and good copolymer solubility, but makes the influence of the DA interactions on the chain microstructure (tacticity and sequence distribution) to be negligible.

The small value of association constant determined from the composition dependence of proton chemical shifts for copolymers in solution is confirmed by the very weak modifications in IR absorption spectra obtained from polymers in solid state.

There are reasons to suppose that the DA interactions in the studied polymers determine formation of separated pairs of 1:1 associates and not ..DADADA.. stack sequences.

The dependence $T_g(f_A)$ does not correlate with those of molecular mass and size. The weak deviation of the glass transition temperature from the weighted temperature of the corresponding homopolymers can be described by a model based on the kinetics of association and considering a similitude between the DA interactions and the crosslinks.

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