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Mobility of knots in polyethylacrylate networks.

Fluorescence anisotropy measurements

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Summary

The steady state fluorescence anisotropy of the chromophore dialkylbenzene, which constitutes the crosslinks of polyethylacrylate and polymethylmethacrylate networks, has been investigated over a range of temperatures, from -20 to 80 °C. In polymethylmethacrylate networks the limit anisotropy of dialkylbenzene (r_0 = 0.198) and vinylphenyl side groups of the elastic chains (r_0 = 0.304) have been determined by applying a correction method (previously reported) to discount artifacts typical of front face excitation. In polyethylacrylate networks it was found that the mobility of knots does not change appreciably with temperature even 100 °C above the glass transition of the system (about -10 °C). It was concluded that polymer dynamics that affect the mobility of knots is different of that determining the motions of the elastic chains.

Introduction

Fluorescence measurements provide unique information on the segmental mobility of polymeric systems in a given environment (1,2). If the chromophore is labeled to a polymer chain, the chromophore mobility is related with polymer relaxation mechanisms which take place in the nanosecond time scale. If the chromophore is embedded in a polymer matrix, its mobility is related with the free volume of the sample, whether it is rubber or glass.

Monnerie (2-6) was pioneer in applying the fluorescence anisotropy technique to study the temperature dependence of segmental motions above and below the glass transition temperature. Several other articles (7-9) have been published on the mobility of probes and labels joined to linear or crosslinked polymers (6,10,11) and its temperature dependence.

The aim of this work is to determine the mobility of the crosslinks in dry polyethylacrylate networks (PEAN) above the glass transition temperature. Using divinylbenzene as crosslinker we get knots which are at the same time a chromophore (dialkylbenzene) whose anisotropy can be measured by front face excitation. To calculate the mobility parameter it is necessary to know precisely the limit anisotropy of the chromophore and with that purpose we have also measured at several temperatures the anisotropy of the same chromophore, dialkylbenzene, in polymethylmethacrylate networks (PMMAN) crosslinked also with divinylbenzene. The glass transition temperature of PMMAN is well above the temperatures of the experiment and it can be assumed that rotational depolarization is totally avoided.

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Experimental Section

Polyethylacrylate (PEAN) and polymethylmethacrylate (PMMAN) networks were synthesized in bulk by radical polymerization with 0.03% (w/w) α,α'-azo-bis-isobutyronitrile (AIBN) as initiator and divinylbenzene as crosslinker. The reaction proceeded at 70 °C for PEAN and different temperatures from 50 to 120 °C were employed for PMMAN along polymerization to get transparent thin discs. AIBN, from Fluka, was twice recrystalized in methanol. Ethylacrylate and methylmethacrylate, from Fluka, were twice distilled under reduced pressure. DVB was a technical mixture from Fluka having almost 50% ethylvinylbenzene and small quantities of diethylbenzene; it was purified following the method described in ref. 12 to get 95% divinylbenzene containing mainly *o*- and *m*- isomers, in accordance with ^{1}H NMR measurements. PEAN were repeatedly washed with dioxane of high quality (spectrophotometric grade, from Carlo Erba) until solvent gave no signal of any dissolved material.

The average molecular weight of chains between crosslinks (M_c) was calculated for PEAN's from gravimetric measurements of the maximum swelling ratio (*S*) in acetone. It was determined twice for each sample and the average was given (Table 1). The equilibrium was achieved after one week at room temperature, about 20 °C. The polymer-solvent interaction parameter (χ= 0.41 at 20 °C) was calculated from data in ref. 13.

Steady state fluorescence measurements were performed by front face excitation in a SLM-AB2 spectrofluorimeter fitted with Glan-Thompson prisms polarizers. The excitation wavelength was set at 260 nm. The anisotropy, $r(\lambda)$, was calculated at each emission wavelength to detect the existence of artifacts due to adventitious light scattering (14) and to determine the interval of incertitude associated with r measured on the anisotropy spectrum at the minimum. $r(\lambda)$ was determined as:

$$r(\lambda) = \frac{I_{II}(\lambda) - I_{\perp}(\lambda)G(\lambda)}{I_{II}(\lambda) + 2I_{\perp}(\lambda)G(\lambda)} \qquad (1)$$

where $I_{||}(\lambda)$and $I_{\perp}(\lambda)$ represent the intensities measured when the transmission axis of the polarizer is oriented vertically and that of the analyzer is parallel (vertical) or perpendicular (horizontal), respectively, to it. G is a grating correction factor; it was calculated for each wavelength as the ratio of the emission intensities measured when the transmission axis of the polarizer is horizontal and those of the analyzer are vertical and horizontal, respectively. Error bars in plots represent the fluctuations of the anisotropy in the minimum around the average value.

Temperature ramps were made from the lowest temperature to the highest one. Then, the sample was slowly cooled to room temperature and anisotropy was measured again; these results are plotted as filled points and they show that samples do not suffer degradation or hysteresis. Temperature was measured on the sample and it was controlled with oscillations of less than 0.2 °C.

Table 1.-Molecular weight between crosslinks (M_c), swelling ratio in grams of acetone retained in the equilibrium per gram of dry gel (S) and glass transition temperature of polyethylacrylate networks.

SAMPLE	$M_c/10^3$	S(g/g)	T_g(°C)
PEAN4	4	3.11	- 6.8
PEAN65	65	13.36	-12.7

Results and Discussion

Divinylbenzene is commercialized like a mixture of the *o*-, *m*- and *p*- isomers of diethylbenzene, ethylvinylbenzene and divinylbenzene. Purification by methods described in ref. 12 allows to isolate *o*- and *m*- isomers of divinylbenzene and an small fraction of ethylvinylbenzene. After crosslinking polymerization with purified divinylbenzene there are in the network several chromophores: i) an small fraction of ethylphenyl side groups derived of ethylvinylbenzene monomers; their contribution can be considered negligible and they won't be taken into account; ii) most of the chromophores would be phenylene groups anchored to chains by two sides and acting as effective knots of the network; iii) an small fraction of divinylbenzene monomers would react only by one vinyl and therefore they would remain in the network as pendant vinylphenyl groups.

Fig. 1 shows the fluorescence spectra of purified divinylbenzene and that of models for effective knots (*o*-diethylbenzene, DEB) and vinylphenyl side groups (*p*-methylstyrene, MVB) of the elastic chains in PEAN or PMMAN. The emission of chromophores in knots must be expected to be centered at about 290 nm and that of side groups at about 310 nm.

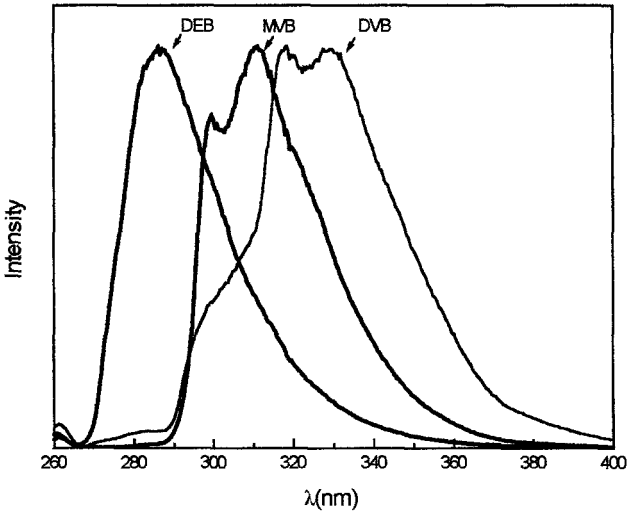

Figure 1.- Fluorescence spectra of *o*-diethylbenzene, *p*-methylstyrene and divinylbenzene in dilute solution at r.t. Excitation wavelength: 260 nm in any case.

In accordance with this, the fluorescence spectra of PEAN and PMMAN (Fig. 2) peaks at about 290 nm with a shoulder in the red side. Fig. 2 shows how the total emission spectrum of PMMAN can be decomposed in two bands, one of them due to dialkylbenzene (effective knots) and the other, (the difference of the total spectrum and that of the model *o*-diethylbenzene normalized at 280 nm), which having a maximum at 312 nm can be ascribed to pendant vinylphenyl groups. Taking into account the difference of fluorescence quantum yields of the two chromophores, the proportion of pendant vinylphenyl groups can be determined (15).

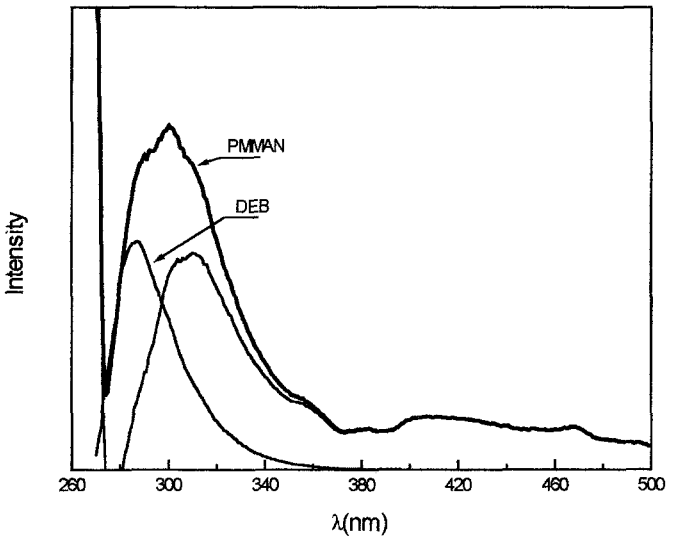

Figure 2.- Fluorescence spectra of PMMAN and *o*-diethylbenzene normalized at 280 nm and difference of both.

It has already been pointed out (14) that in determining the anisotropy of an emission it is very important to run the whole anisotropy spectrum and, if necessary, to apply corrections for overlap of Rayleigh scattering and stray light with fluorescence. Fig. 3 show both the fluorescence and anisotropy spectra of PMMAN at different temperatures. Upon increasing temperature the stray light remains about flat and constant but fluorescence intensity decreases and therefore, *f*, the fraction of spurious light at the wavelength of the maximum emission increases. The anisotropy spectra show two short but well resolved plateaus at around 290 and 310 nm, the maxima of the two bands (Fig. 2) forming the total emission spectrum. At the wavelength of Rayleigh light scattering and at the red side of the spectra, where emission becomes negligible, the anisotropy tends, as expected, to 1.

At temperatures well below the glass transition temperature of the matrix, the anisotropy of a chromophore should be constant and equal to the limit anisotropy r_0. Since the anisotropies of the plateaus in Fig. 3 change slightly with temperature it must be concluded that correction for light scattering artifacts are necessary. Figs. 4 and 5 show

how the experimental and corrected anisotropies of the two plateaus change with the relative contribution of stray light.

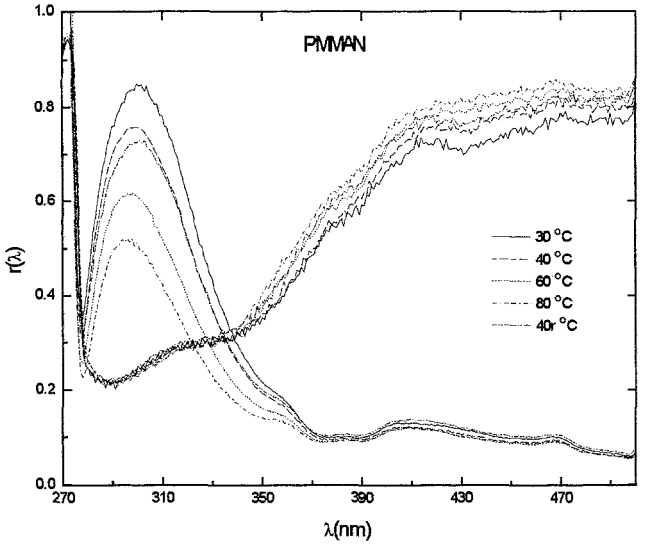

Figure 3.- Fluorescence and anisotropy spectra of PMMAN at different temperatures. Excitation wavelength 260 nm.

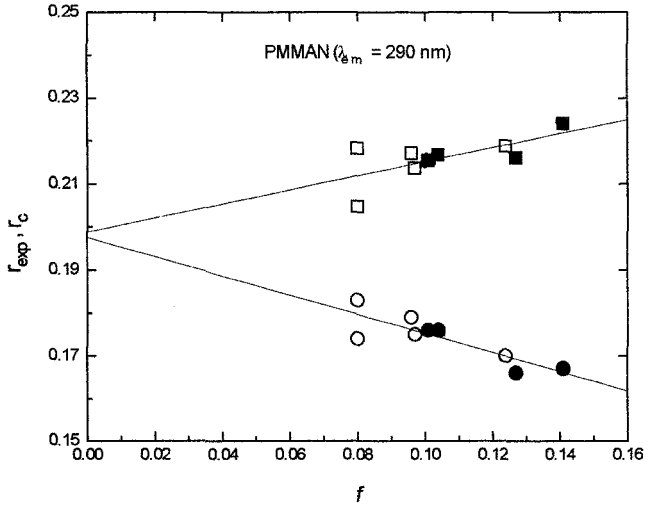

Figure 4.- Experimental and corrected anisotropies of dialkylbenzene in PMMAN as a function of the fraction of stray light. Different symbols correspond to different sets of experiments made with different excitation and emission band-pass.

The experimental anisotropies (r_{exp}) are the average of those measured in the range 280-300 nm for dialkylbenzene and 310-320 nm for alkylvinylbenzene and error bars (or the size of the symbol employed) represent the corresponding standard deviation.

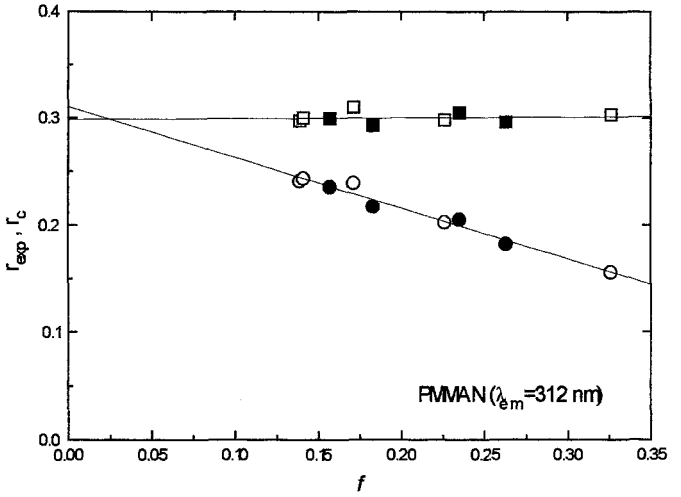

Figure 5.- Experimental and corrected anisotropies of alkylvinylbenzene in PMMAN as a function of the fraction of stray light. Different symbols correspond to different sets of experiments made with different excitation and emission band-pass.

Corrected anisotropies (14) are calculated with the following expression:

$$r_c = \frac{3r_{exp} - f\left[1 + 2r_{exp}\right]}{3 - f\left[1 + 2r_{exp}\right]} \qquad (2)$$

As expected (14), the dependence of r on f is about linear and the r values extrapolated to f=0 are r_0=0.198 for dialkylbenzene (effective knots) and r_0=0.304 for alkylvinylbenzene side groups.

No plateau at 310 nm is observed in the anisotropy spectra of PEAN, indicating that the percentage of vinylphenyl side groups is negligible. The anisotropy of dialkylbenzene groups has been determined on the plateau at 290 nm as above indicated. Figs. 6 and 7 show the temperature dependence of the emission anisotropy of the effective knots in PEAN4 and PEAN65 respectively.

It can be observed in Fig. 6 that experiments made in different days and with different slits give the same trend, the anisotropy remains about constant with temperature. From the dependence on f, the fraction of stray light for each slit, it can be calculated for each temperature the anisotropy extrapolated at f=0 which appears also in Fig. 6. The difference of the intercept at f=0 for the experimental and corrected values of the anisotropy is less than 5%.

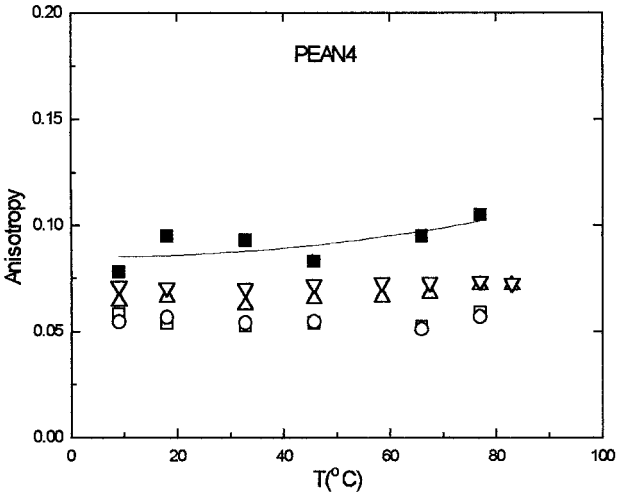

Figure 6.- Anisotropy of PEAN4 at 290 nm as a function of temperature measured with four different slits and extrapolated to $f = 0$.

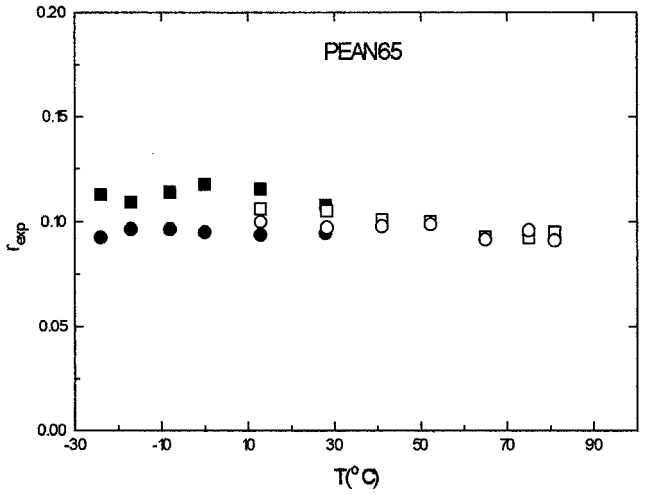

Figure 7.- Anisotropy of PEAN65 at 290 nm as a function of temperature measured with different slits and in two set of experiments at low and high temperatures.

It is well known (1) that the emission anisotropy of probes and labels in linear or crosslinked polymer matrix, decreases upon increasing temperature above the glass

transition temperature. Nevertheless, the emission anisotropy of dialkylbenzene in PEAN's is about constant with temperature and even increases slightly. The emission anisotropy is related (4) with the chromophore mobility (*m*) through the expression:

$$m = \frac{r_o}{r} - 1 \qquad (3)$$

Thus, it can be said that, usually, the mobility of probes and labels in polymer systems increases from zero to infinitum at temperatures above T_g and surprisingly, the mobility of knots in PEAN is relatively large but insensitive to temperature or degree of crosslinking in the network (Fig. 8).

Since the fluorescence lifetime of dialkylbenzene changes only slightly with temperature (15) going from 13 to 10 ns in the rage of temperatures 5-100 °C, it must be concluded that rotations of knots take about the same time than the chromophore fluorescence lifetime (*m*~1) in the hypothesis of isotropic movements and that they do not change much with temperature or the degree of crosslinking. This would be in contradictions with previous contributions (11) which concluded that polymer dynamics is the same in the elastic chains and in crosslinks but in that case (11) the knot was labeled with a chromophore joined by a flexible spacer and that would may be change the chromophore mobility.

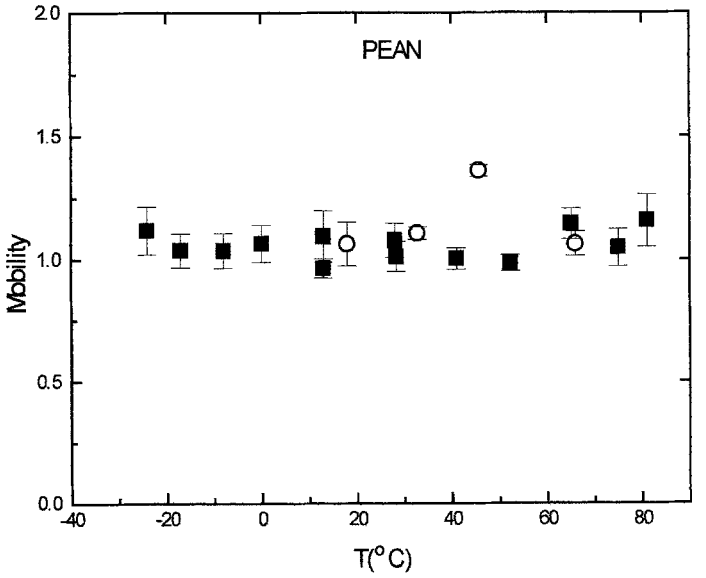

Figure 8.- Mobility of knots in PEAN4 and PEAN65 as a function of temperature. Points with standard deviation larger than 10% of PEAN4 have been suppress.

A mobility equal to 1 is reached for an anthracene probe in a polymer matrix at about 60 ºC above T_g and it was necessary to get temperatures of T_g +100 ºC to get the same mobility for larger probes (4). The size of the chromophores plays an important role in their mobility at T_g, temperature at which *m* can be larger than zero. This would explain the relatively large mobility of PEAN knots which are formed by the smallest chromophore, just a phenylene ring.

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