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# Relaxations of Poly(methyl methacrylate) Probed by Covalently Attached Anthryl Groups

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ABSTRACT: The molecular relaxations of poly(methyl methacrylate) (PMMA) were studied using three different techniques: DSC, DMTA, which are sensitive to bulk properties, and the variation of fluorescence emission with temperature, a molecular sensitive method. Because this is a nonfluorescent polymer, we synthesized copolymers of methyl methacrylate with several contents of 9-methylanthryl methacrylate. The increase in the spacing between each anthryl group brought about a gradual decrease in $T_g$ of the copolymers, leveling out at about 30−40 PMMA mers, indicating that the minimum spacing to attain the PMMA glass transition was situated in this length range. The fluorescence emission of a copolymer with 98 MMA units interspersed between each chromophoric unit was proved to be mechanically equivalent to PMMA homopolymer and was used to probe macromolecular motions involving shorter segments: apart from the main transitions commonly found for PMMA (α and $\beta$), the other two were detected at lower temperatures ($\gamma$ and $\delta$). Apparent activation energies for all relaxations using both techniques are also reported and discussed.

## 1. Introduction

The temperature-dependent relaxation processes in polymeric materials have been extensively studied, and the number of published works in the subject has increased in recent years. A variety of techniques have been employed to examine relaxation processes, including dielectric and dynamic mechanical analyses,[1−4] NMR spectrometry,[5] positron annihilation,[6] and fluorescence spectroscopy.[7,8]

It is customary to label relaxation transitions in polymers as α, $\beta$, $\gamma$, $\delta$, etc., in alphabetical order with decreasing temperature. In poly(methyl methacrylate) (PMMA) the highest temperature relaxation, the α relaxation, is the glass transition process ($T_g$) and is ascribed to long-range conformational changes of the polymer backbone. Cooling through $T_g$ produces a nonequilibrium thermodynamic conformational distribution, which slowly attempts to reach an equilibrium value appropriate to the annealing temperature. Comparative studies with similar polymers have attributed the secondary $\beta$, $\gamma$, and $\delta$ relaxations to the side-chain motions (flips) of the ester group and rotation of methyl groups attached to the main chain and side chain, respectively.[9] Results obtained with NMR techniques for PMMA revealed that both the dynamic of the ester moiety and the methyl groups ($\beta$-relaxation) may be coupled with main-chain motions (α-relaxation).[5,10−15]

Differential scanning calorimetry is based in variations of the specific heat, $C_p$, with temperature. Long-range segmental motions as the glass transition bring about changes in $C_p$ that can be detected, and DSC is a widespread technique for this measurement. On the other hand, short-range motions do not provide variations in $C_p$ large enough to be sensed by DSC. Dynamic mechanical and dielectric spectroscopy are bulk methods that can probe short-range molecular motions. The latter is a particularly sensitive method.[16]

Despite the extensive work undertaken, the origin and the nature of the molecular motions involved in those relaxations and the glass transitions is not yet fully clarified, and one of the possible reasons is that motions in polymer chains are strongly coupled. For example, even though the $\beta$-relaxation takes place at lower temperature, quantitative analysis by NMR demonstrated that in the glassy state only about one-third of the side groups undergo slow 180° flips.[17]

As part of an effort to obtain experimental data that can be compared against conformational energy calculations, we have prepared a series of PMMA labeled with systematically spaced 9-antryl methyl groups. Figure 1a depicts the structure of the labeled PMMA, namely poly(methyl methacrylate-*co*-9-methylanthryl methacrylate), P(MMA-*co*-MMAnt).[18] The anthryl moiety was introduced in the polymer chain to provide two important porperties: one is photoluminescence because PMMA is not intrinsically fluorescent and the other is electroluminescence, since this property arises when the anthryl groups are set in appropriate concentrations.[18] Figure 1b gives an idea of the bulkiness and the relative orientation of the 9-anthrylmethyl methacrylate substituent in relation to the main chain.

The fundamental assumption for employing luminescence as a technique for detecting polymer relaxation processes is that the mobility of the immediate environment around the lumophore increases the efficiency of

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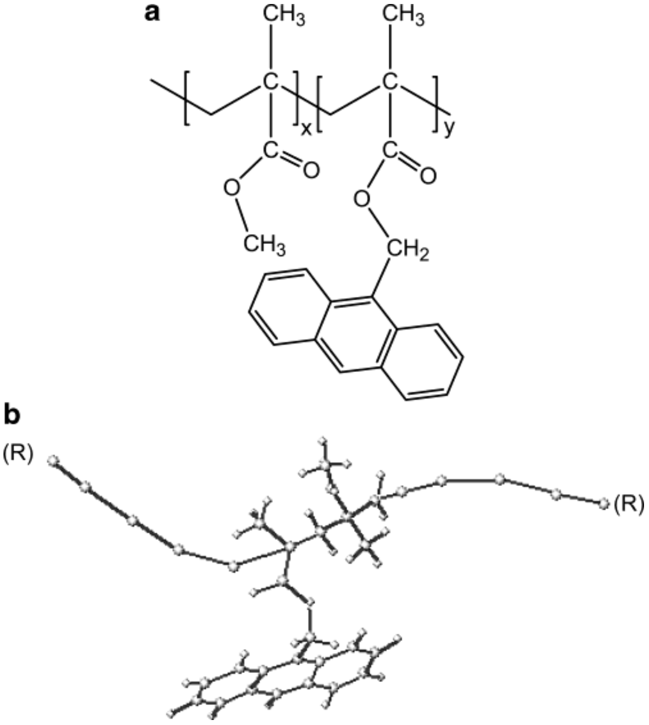

**Figure 1.** (a) Chemical structure of poly(MMA-*co*-MMAnt). $x = 98, 35, 25, 10, 4, 2, 0$; $y = 1$. (b) Optimized geometry of a MMA−MMAnt linkage. The (R) represents the main chain.

nonradiative processes.[8,12,14,15,19−25] The sensitivity of the fluorescence intensity on the polymer relaxation processes can be explained by the ability of the media to dissipate thermally the nonradiative energy from the fluorescence moiety. At lower temperatures, where the medium is completely frozen, the fluorescence takes place from non-relaxed Franck−Condon states. This emission is in general observed at higher energy where the emission band is usually sharper. On the other hand, when the polymer matrix undergoes some relaxation process, the solvation layer around the excited-state lumophore can be reoriented around the new dipole moment, the fluorescence is emitted from a relaxed Franck−Condon state, and as a result, a spectral red shift and broader bands assigned to the several possible conformations are observed.[20,24] Therefore, the fluorescence intensity depends on intrinsic properties of the molecule (radiative and nonradiative rate constants) as well as extrinsic properties, as the ability of the medium to dissipate the energy transferred from the excited-state fluorophore.

Several reports have demonstrated that the electron−phonon coupling model can be employed for describing the ability of the medium to dissipate the lumophore energy and that the efficiency of the coupling depends on the polymer relaxation processes.[23] Thus, there are at least three experimental evidences supporting assignments of the relaxation temperatures of polymer chains from the steady-state emission spectra of fluorescent probes (physically dispersed or covalently bound to the polymer chain): peak position, fluorescence intensity, and full width at half-maximum. If a fluorescent group is attached to a polymer segment directly involved with a relaxation mode, polymer mobility and fluorophore deactivation will be strongly correlated events.[5,8,19−21,25] This is due to the strong coupling between the polymer motion and the fluorescent moiety and to the already mentioned enhancement of the efficiency of the nonradiative processes, inducing a decrease of the emission intensity, brought about by the mobility of the polymer chain in the immediate environment of the fluorescent moiety. As a result, any changes in the observed fluorescence spectral profile or integrated intensities can be directly related to local changes in the polymer matrix.

In this work the PMMA relaxations were probed by thermal techniques (DSC, DMTA), which are sensitive to bulk properties, and by variation of fluorescence emission with temperature, a molecular sensitive method. The thermal transitions in polymers occur at different temperatures and with different activation energies that depend on the size and intermolecular interactions of the set of segmental motions involved. The study through several techniques can lead to a static and dynamic picture of a polymer; however, the kinetic description of relaxation processes obtained from diverse techniques is based on different rheological models.[8,21,25] Thus, apparent activation energies for processes detected by different methods are expected to be different.[8,21,25]

## 2. Experimental Section

**Copolymer's Synthesis.** Materials: Methyl methacrylate (MMA, Nitriflex Co.) was washed twice with 5% aqueous NaOH and twice with distilled water, dried overnight with $CaCl_2$, filtered, kept at 278 K over $MgSO_4$ for 24 h, and distilled at atmospheric pressure (bp = 373 K), in the presence of hydroquinone and using a copper wire spiral in the column, to inhibit premature polymerization. 9-Methylanthryl methacrylate monomer (MMAnt, Aldrich, PA) was used without further purification. Benzoyl peroxide was recrystallized from methanol.

Films for spectroscopy measurements were cast form chloroform solutions, with thickness of 40−50 $\mu$m. After the solvent evaporation (24 h, 353 K, atmospheric pressure) they were annealed at 350 K in an oven under dynamic vacuum ($10^{-4}$ mmHg) for 1 day. There are some experimental evidences that under this condition any residual solvent was completely removed: no additional peak has been observed in DSC, and there is no solvent mass loss in thermal gravimetric analysis (not shown). In addition, annealing under these conditions erases the thermal history of the film.

**Polymerization Procedure.** The polymerization was carried out in toluene, typically 20% monomer/solvent (w/v) at 373−378 K. Benzoyl peroxide was used as initiator (1% peroxide/monomer w/w). The comonomer feed ratio was adjusted according to their reactivity ratios, which were determined through the Finemann−Ross and Kelen−Tudös methods, as described elsewhere.[27] After reacting for 24 h, the polymerization mixture was poured over 10 times the volume in methanol, and the precipitated material was filtered and dried overnight in a vacuum oven at 310 K.

**Composition Determination.** The quantitative evaluation of the anthryl content in the copolymer, poly(MMA-*co*-MMAnt), was performed using a calibration curve built with UV−vis spectroscopy data using the $\lambda = 368$ nm band absorption of anthracene.[18]

**Steady-State Fluorescence Emission.** Steady-state fluorescence spectroscopy, in temperature range from 40 to 410 K, of samples in form films were performed using an instrument described previously.[28] A slice of a film (0.5 cm × 0.5 cm) was sandwiched between quartz disks and inserted into the cryosystem. Spectra were recorded at several temperatures at intervals of 10 K by heating rate the sample under dynamic vacuum ($10^{-4}$ Torr). The excitation wavelength was $\lambda_{exc} = 368$ nm, and the emission was collected from $\lambda_{em} = 380$ to 500 nm at 1 nm intervals.

**DSC.** The runs were performed in Netzsch 200 equipment in open aluminum pans under nitrogen flux. Samples of about 5 mg were submitted to a heating rate of 10 K/min up to 500

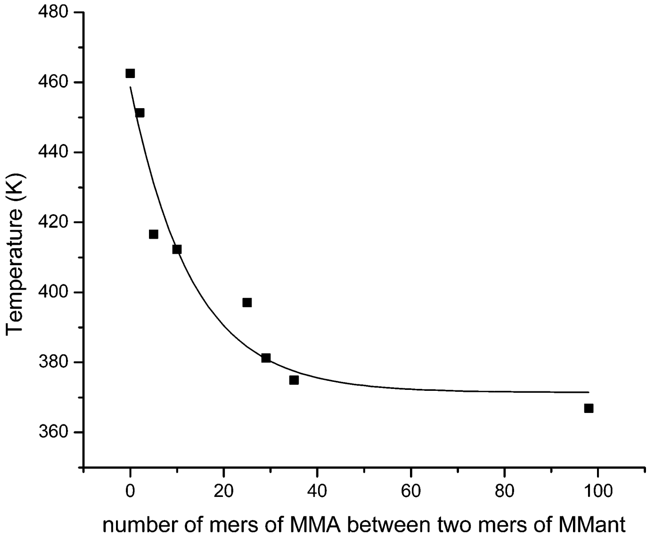

**Figure 2.** Dependence of the glass temperature on copolymers' composition.

**Table 1. Glass Transition Temperature of PMMA, PMMAnt, and Copolymers Poly(MMA-*co*-MMAnt); Data from DSC**

| molar ratio MMAnt:MMA | PMMA | 98:1 | 35:1 | 25:1 | 10:1 | 4:1 | 2:1 | PMMAnt |
|---|---|---|---|---|---|---|---|---|
| $T_g$ (K) | 373 | 374 | 376 | 398 | 412 | 452 | 462 | 476 |

K in a first run, cooled to 220 K, and heated again at the same rate. The recordings for the first and second runs were essentially identical.

**Dynamic Mechanical Thermal Analysis (DMTA).** A Rheometrics Scientific DMTA V was used to perform tension tests. Each sample was cut from chloroform cast films to a small rectangular sample within the following range of dimensions: length of 23−26 mm, width of 2−8 mm, and thickness of 0.02−2 mm. A strain limit of 0.1% was applied in the temperature range from 170 to 420 K at a heating rate of 2 K/min. Several frequencies were used, as discussed in the text.

## 3. Results and Discussion

The $T_g$ values obtained by DSC are shown in Table 1. The stiffening effect of the anthryl groups is clearly seen by the shift of the $T_g$ values toward higher values as the amount of lateral moieties increases; the energy of activation for rotation of the bulky anthryl groups is, of course, much higher than that of methyl groups. The homopolymer's glass transition reaches values near 470 K while value for PMMA was 373 K.

The decrease in $T_g$ with increasing the spacing between each anthryl group is gradual until about 30−40 methyl methacrylate groups are interspersed, as shown in Figure 2. This indicates that the minimum spacing to attain the PMMA glass transition is situated in this length range, and the polymer becomes insensitive to the presence of anthryl groups. This fact was used to produce a copolymer thermally and mechanically equivalent to PMMA homopolymer, enabling the use of the chromophore as a probe to sense PMMA relaxations.

Measurements of the loss modulus ($E''$) at several frequencies were made for PMMA vs temperature, and curves for three frequencies are shown in Figure 3. Both α- and $\beta$-relaxations have been analyzed through the Arrhenius law

$$f = f_0 \exp(-E/RT) \tag{1}$$

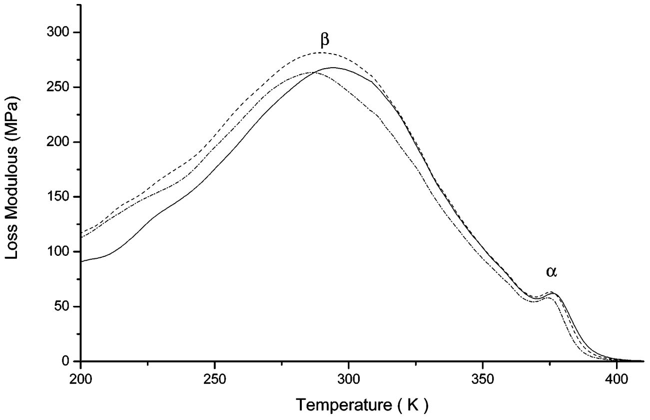

**Figure 3.** Temperature dependence of loss modulus ($E''$) for several frequencies for poly(methyl methacrylate): (− • • −) 1.0, (− − −) 2.0, and (−) 3.3 Hz.

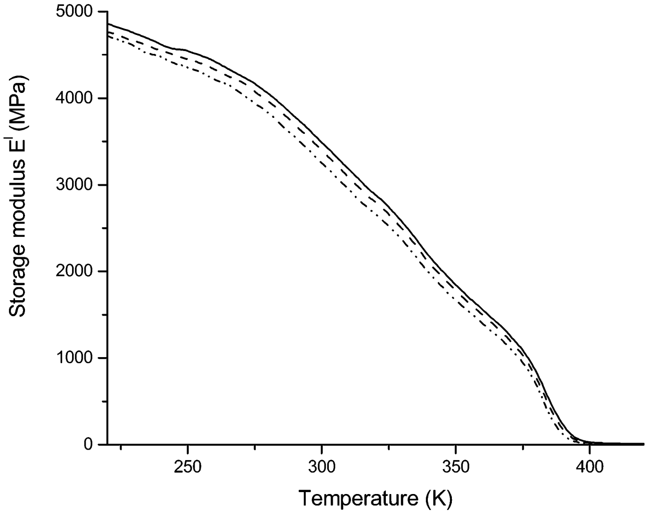

**Figure 4.** Temperature dependence of storage modulus ($E'$) for several frequencies for poly(methyl methacrylate): (− • • −) 1.0, (− − −) 2.0, and (−) 3.3 Hz.

where $f$ is the frequency (Hz), $f_0$ is the preexponential factor (Hz), $E$ is the activation energy (J mol$^{-1}$), $T$ is the absolute temperature (K), and $R$ is 8.32 J K$^{-1}$ mol$^{-1}$.

The temperature for $\beta$-relaxation, associated with side-chain motions of the ester group, detected in loss modulus plots, was located at 286, 289, and 296 K at 1.0, 2.0, and 3.3 Hz, respectively, The relaxation maxima were accompanied by decreases of storage modulus, $E'$, as shown in Figure 4. The calculated values of the apparent activation energy ($E_a$) for the $\beta$ relaxation provided a value of 83 kJ mol$^{-1}$. The preexponential factor is near the Debye frequency, $f_0 = 10^{15}$ Hz.[29] For the $\beta$ maximum of PMMA which is observed mechanically at around 280 K and 1 Hz, and dielectrically at around 320 K and 60 Hz, the respective activation energies $E_a$ were 70 and 85 kJ mol$^{-1}$, respectively.[30] It is generally believed that this maximum is due to the hindered rotation of the $-COOCH_3$ group about the C−C bond linking it to the main chain.

The α-transition peaks were located at 374, 376, and 378 K at 1.0, 2.0, and 3.3 Hz, respectively. The calculated values of the apparent activation energy $E_a$ and the preexponential factor were $E_a = 353$ kJ mol$^{-1}$ and $f_0 = 10^{49}$ Hz. Such high values of the activation energy and preexponential factor indicate that the α relaxation originates from complex and correlated molecular motions, as expected for the glass transition.[9]

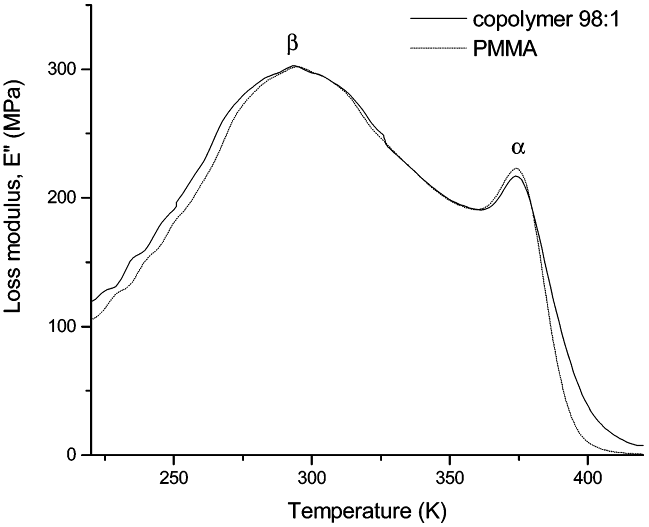

**Figure 5.** Temperature dependence of loss modulus ($E''$) for poly(methyl methacrylate) and poly(methyl methacrylate-*co*-9-methylanthryl methacrylate) (98:1). Frequency = 3.3 Hz.

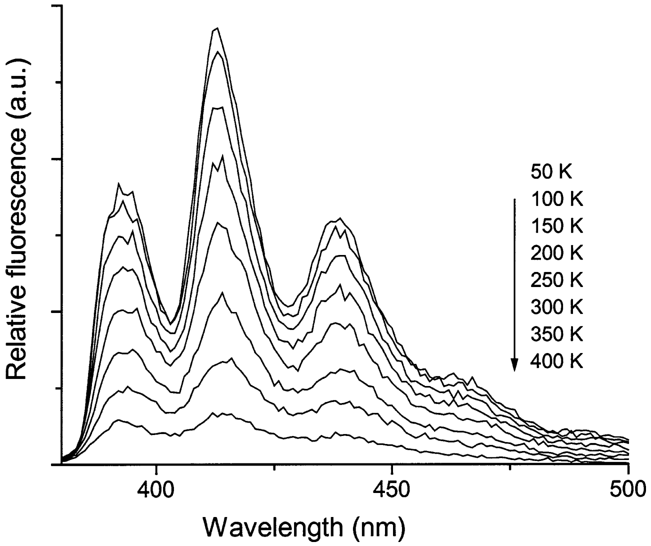

**Figure 6.** Fluorescence spectra of the probe (anthryl group) in poly(methyl methacrylate-*co*-9-methylanthryl methacrylate) (98:1) at several temperatures.

Figure 5 shows the loss modulus vs the temperature graph for PMMA and copolymer 98 ($x = 98$ in Figure 1). It was observed that in this composition range the anthryl groups, in accordance with DSC results of Figure 2, did not affect the mechanical properties. Since both the thermal and the mechanical properties of this copolymer are equivalent to PMMA, the dependence of the fluorescence intensity of the anthryl groups was used as an attempt to follow local changes that accompany the onset or cessation of those various relaxation processes that occur in PMMA films between 40 and 410 K.

Figure 6 shows the fluorescence spectra at several temperatures for films of the copolymer 98 (one anthryl for each 98 MMA mers). The shape and peak positions of the emission are usual for anthryl moieties attached to a polymer chain. Apart from the decrease of the intensity, the spectral profile practically did not change when the lumophore is linked to the PMMA as already found when the chromophore was linked to other polymers, such as polyethylene.[8,18,19,26] Apparently some trivial energy transfer process takes place since the relative intensity of the 0−0 vibronic band ($\lambda_{em}$ = 438 nm) is lower than the 0−1 band ($\lambda_{em}$ = 412 nm). Furthermore, the fluorescence intensity decreases with the increase of the temperature, as expected for systems controlled by intrinsic (temperature dependence of all nonradiative rate constants of the fluorophore in the electronic excited state) and by extrinsic effects (fluorophore/polymer interactions and polymer relaxation processes).[8,12,14,15,19−21,23−25]

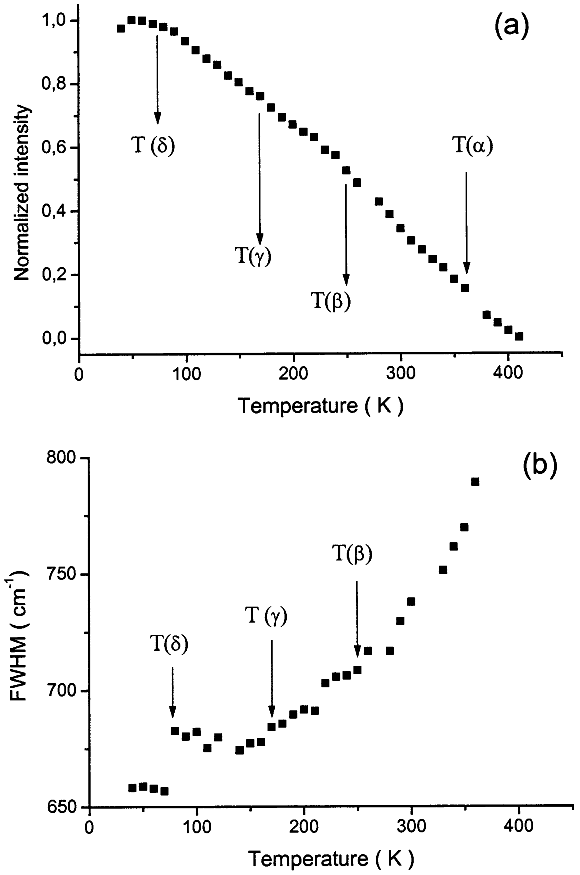

**Figure 7.** (a) Integrated and normalized fluorescence intensities for poly(methyl methacrylate-*co*-9-methylanthryl methacrylate) (98:1 molar ratio) vs temperature. (b) Full width at half-maximum (FWHM) of the 0−0 band at the same temperature range.

Plots of the integrated fluorescence intensity (defined as the entire area under the spectral profile, Figure 6) versus temperature (50−410 K, Figure 7) exhibited slope changes near the transition temperatures for relaxation processes identified previously by either DMTA or DSC. In this plot the integrated intensity is also normalized considering the higher intensity as the unit. Thus, the plot in Figure 7a depicts how the intensity decreases as the temperature increases. As already discussed, the full width at half-maximum (FWHM) is a measure of the interaction among the emitting species and their environment. The FWHM values were obtained by deconvolution of the entire fluorescence spectrum using Gaussian functions. Five peaks were employed. We considered the best fit when the whole spectrum is recovered, the $\chi^2$ was minimized, and a random distribution of residuals was produced. The plot of the temperature dependence of the FWHM (Figure 7b) indicated the following: (i) The fluorescence spectra of the polymer bound anthryl groups were broader than that of the isolated group. It is a common fact that the emission of chromophores covalently at-

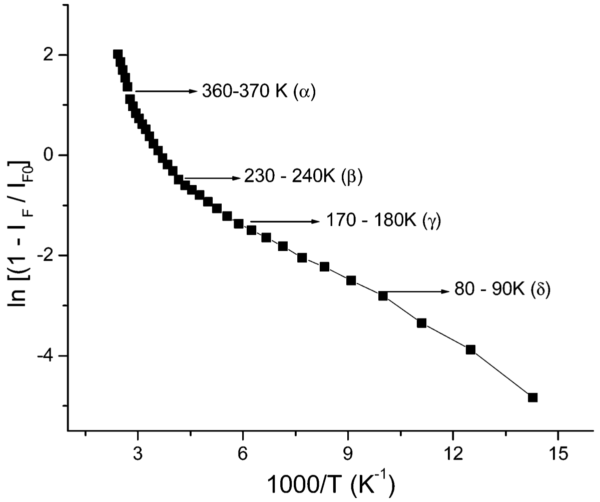

**Figure 8.** Arrhenius-type plots for $\ln[1 - I_F/I_{F_0}]$ vs $1000/T$. Data from Figure 7.

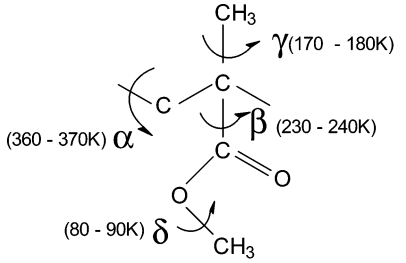

**Figure 9.** Illustration of the relaxations detected in PMMA through the technique of fluorescence emission with the variation of the temperature.

tached to a polymer backbone is always broader than the same compound as molecular guest in a polymer host. This effect was attributed to the presence of several possible fluorophore conformers.[8,20,24,26] (ii) FWHM at lower temperatures is narrower and gradually become broader at higher temperatures because the decays take place from more relaxed Franck–Condon states. (iii) The extrapolated broadening to 0 K (660 $cm^{-1}$) is larger than for organic crystals or for host/guest systems with similar decay rate (5–10 ns),[18,26] indicating larger conformational disorder.

The fluorescence intensity data can also be represented according to the Arrhenius-type plot as shown in eq 2 (Figure 8). This aids in the location of onset transition temperatures and allows us to calculate the apparent activation energies:

$$1 - \frac{I_F(T)}{I_F(0)} = A \exp\left(-\frac{E_A}{RT}\right) \qquad (2)$$

where $E_A$ is the activation energy for the complex relationship between the ratio of radiative and nonradiative processes of the excited-state moiety, which are intrinsic processes, and the polymer relaxation processes, which are extrinsic processes.

The criterion for defining the temperature of a specific relaxation process involved the simultaneous analyzing of the three types of plots: the integrated and normalized intensity (Figure 7a), the FWHM (Figure 7b), and the Arrhenius plot (Figure 8). In each one of these plots we defined the change of the slope and thus the relaxation temperature in the strict condition that the new slope is maintained for the next three values of the parameter (integrated intensity, FWHM, or the $\ln[1 - I_F(T)/I_F(0)]$). In addition, we considered a relaxation temperature when the values of these three successive points differ from the average distribution of the previous values. To classify the relaxation processes, they were named as indicated in Figure 9, in order of increasing temperatures.[5,10–15]

From these three plots it became clear that fluorescence could probe more subtle molecular motions that are not detected in mechanical or thermal essays either because the bands are very broad or the temperature range was not covered. As previously shown, in DSC and DMTA runs the lowest temperature attained was 150 K. As shown in Figure 7a, the fluorescence intensity was virtually constant for $T < 90$ K ($\delta$-relaxation), and above this temperature three slope changes could be detected, with onset at 170–180, 230–240, and 360–370 K, which correspond to temperature ranges where the $\gamma$-relaxation, $\beta$-relaxation, and the $T_g$ (α-relaxation), respectively, have been already observed. These slope changes were observed in similar temperature ranges for the FWHM plot (Figure 7b).

The onset of the transition temperatures in the Arrhenius plot is assigned by joining linear regions with significantly different slopes.[8,12,14,15,19–21,23,25] Linear segments of Arrhenius plots of emission intensities extend over a temperature range until the onset of the new thermal activated process. Thus, we are explicitly assuming that with increasing temperature the polymer relaxation processes commence successively, being additive when the chains undergo more cooperative motions; for example, the slope region above $T_\gamma$ should be proportional to the combined activation energy from both the $\delta$ and $\gamma$ relaxations. Consequently, similar to the other techniques, the relaxation process detected by fluorescence spectroscopy is a complex cooperative motion, and the experimental temperature data are not a well-defined value.

Four types of activation barriers have been identified for the relaxation processes: the lower temperature process ($\delta$-relaxation), $T_\delta = 80–90$ K, was attributed to rotation of the methyl group of the ester group,[9,31] with an apparent activation energy of 2.8 kJ $mol^{-1}$.

The next slope change, the $\gamma$-relaxation, observed around 170–180 K, was attributed to the relaxation associated the rotation of the methyl group bound to the main chain,[31] with an apparent activation energy of 3.7 kJ $mol^{-1}$. Molecular mechanics calculations[30] found values ranging from 1 to 7 kJ $mol^{-1}$ at 150 K, whereas NMR results are in the range of 10 kJ $mol^{-1}$.[32] These values are lower than those found from inelastic neutron scattering experiments (29.1 kJ $mol^{-1}$),[33] NMR of pure syndiotactic PMMA (23.3 kJ $mol^{-1}$),[33] and molecular mechanics calculations (28 kJ $mol^{-1}$).[30,34] The calculated value observed in this work is very similar to that found for the $\gamma$-relaxation (motions of short segments and small branches) by fluorescence emission of anthryl groups linked to polyethylene (from 5.4 to 3.0 kJ $mol^{-1}$).[8]

The $\beta$-relaxation, around 230–240 K, was attributed to motions of the ester moieties in poly($n$-alkyl methacrylate)s according to the majority of published data.[30,35,36] The hindrance to this rotation mainly arises from interactions with the main chain methyl groups of the adjacent units. The activation energy found for this transition was in the range of 10.1 kJ $mol^{-1}$. Again, this value is lower than those reported using DMA, 81.1,[35] 75,[30] and 83 kJ mol$^{-1}$ (this work), but is nearer to results from thermally stimulated current (TSC) (41.8−46 kJ mol$^{-1}$).[36] In addition, it was recently reported[17] that the $\beta$-process in PMMA occurred by preferential flip of the side group and was coupled, to some extent, with the main chain motions ($\alpha$-process). The coupling mechanism between $\alpha$- and $\beta$-processes in poly(*n*-alkyl methacrylate)s has been studied considering several types of experimental techniques and the relative importance of the *n*-alkyl side groups.[5,10,37]

The higher temperature relaxation 360−370 K determined from the temperature dependence of the fluorescence emission was ascribed to $\alpha$-relaxation ($T_g$) and was interpreted as coupled main-chain and side-group motions. The corresponding activation energy obtained from the Arrhenius plot was 22.4 kJ mol$^{-1}$. This is a remarkably lower value compared with those determined from the DMTA: $E_a = 353$ (this work), 334,[38] and 200−300 kJ mol$^{-1}$.[39]

Although the location in the temperature scale observed by fluorescence was similar to those found by other techniques, the apparent activation energies were always lower. These discrepancies could be explained taking into account that results from different techniques for the same type of relaxation process reflect differences in the kinetic description of the phenomenon and may be attributed to differences in the nature of the involved processes.[8,21,25] Regardless of the mechanism involved in the fluorescence processes, the apparent activation energies are reflecting how the molecule in the excited state dissipates the energy to the medium. Because the anthryl groups have short lifetimes (few nanoseconds),[18,26] these molecules can only be disturbed by motions of the polymer chain which are in their neighborhood and which are probably moving within the same time scale. Thus, these fluorophores are sensing very localized relaxation processes. Differently, dielectric and dynamic mechanical spectroscopies probe movements of the bulk, with larger amplitudes. Moreover, when we measure the decrease of the fluorescence intensity, what we are really considering is the kinetics of the nonradiative processes, which is enhanced by the increase of the temperature and by the activation of molecular movements within their surroundings. Thus, all apparent activation energies are reflecting the differences of their nature.

The results from these three different techniques have demonstrated that (i) DSC can only detect the glass transition temperature, (ii) DMTA made it possible to detect both the glass transition and the $\beta$-relaxation, and (iii) with the fluorescence data, we could detect not only these two processes but the $\delta$- and $\gamma$-relaxation as well. The location of each specific relaxation was always in the same range, independently of the method used to probe it. Fluorescence is a technique that requires a fluorescent moiety in the polymer chain. This moiety, when added as a guest or when attached to the chain, could disturb the polymer matrix, mainly in its vicinity. Nevertheless, because we are employing a very small anthryl concentration (1/98 units), we are observing mechanically and thermally equivalent materials. We have not observed any changes in the glass transition and/or in the $\beta$-relaxation processes by DSC or DMTA. Thus, although we cannot eliminate this possibility when we are looking for local motions, this disturbance cannot be detected by conventional techniques like DSC or DMTA.

## 4. Conclusions

The synthesis of a series of poly(methyl methacrylate-*co*-9-methylanthryl methacrylate) with systematic variation in monomeric composition allowed the determination of the minimum segment length of methyl methacrylate units to obtain the same glass transition temperature of PMMA, about 30−40 mers. At the same time it was possible to obtain an anthryl-containing structure, which is intrinsically luminescent, which was mechanically equivalent to PMMA homopolymer. This copolymer contained one chromophore interspersed in each 98 MMA sequences. The lumophore was useful as a fluorescence probe to sense PMMA relaxations labeled as $\delta$ (80−90 K), $\gamma$ (170−180 K), $\beta$ (230−240 K), and $\alpha$ (360−370 K). As only the $\alpha$- and $\beta$-transitions were also detectable by thermal mechanical essays at similar temperatures, the fluorescence method proved to be more efficient in probing more subtle relaxations. Although the transition temperatures were located at a similar range by the two methods, the apparent activation energies calculated from the experimental data are very different from each one. This was discussed in terms of the differences in mechanisms involved in the responses provided by the different methods.

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