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Time-Resolved Luminescence Anisotropy Studies of the Relaxation Behavior of Polymers. 1. Intramolecular Segmental Relaxation of Poly(methyl methacrylate) and Poly(methyl acrylate) in Dilute Solutions in Dichloromethane

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ABSTRACT: The intramolecular segmental relaxation behaviors of poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) in dilute dichloromethane solutions have been studied using time-resolved fluorescence anisotropy measurements (TRAMS). TRAMS have been made on two different spectrometers, incorporating a picosecond laser source and synchrotron, respectively, as excitation sources. Excellent agreement was achieved between the resultant relaxation data, generating confidence both in the spectroscopic procedures involved and in the various forms of analytical data retrieval applied. The relaxation characteristics of each polymer, over the temperature range 230−310 K, was adequately described by an exponential model for the anisotropy, for both acenaphthylene- and 1-vinylnaphthalene-based labels. The associated correlation times for segmental motion exhibited an Arrhenius dependence in the temperature range studied, giving activation energies of the order of 14 and 11 kJ mol^{-1} for PMMA and PMA, respectively, in dichloromethane. These values are considerably reduced compared to those which have been reported for either polymer in other solvents. The differences in activation parameters are too great to be explained on the assumption that the solvents function to provide frictional resistance alone to the polymer dynamics. It is tentatively suggested that both PMMA and PMA exhibit specific interactions with dichloromethane and/or other solvents, such as toluene. Alternatively, the naphthyl labels used to interrogate the macromolecular dynamics might experience specific interactions with the dichloromethane which distort the apparent behavior of the polymer.

Introduction

Luminescence techniques have been used to great effect in polymer science. (See, for example, refs 1−3.) Usually, such investigations involve incorporation, at low concentration levels, of a “foreign” luminescent reporter species within the system, either as a label or as a probe. The choice of luminescence approach adopted and whether label or probe be employed depend upon the nature of the information required. Experiments involving simple measurements of emission intensity and/or lifetime and those using probes are limited by their nature, which is essentially vicarious: they report upon the *effects* of changes in polymer behavior upon the photophysical characteristics of the luminescent guest. Anisotropy measurements, on the other hand, using appropriate, covalently bound labels, afford an opportunity for studying macromolecular relaxation behavior, in a direct fashion. (See, for example, refs 4−6.) This is especially true in the case of time-resolved anisotropy measurements (TRAMS). The problem, in the latter instance, lies in recovery, in a reliable manner, of the relaxation information from the emission anisotropy data. (This subject has recently been reviewed. See, for example, refs 5, 7, and 8.)

In the current work, we have studied the intramolecular segmental mobilities of poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) in dilute solution in dichloromethane as a function of temperature. Four different approaches to the recovery of relaxation information have been adopted: impulse reconvolution,[9,10] autoreconvolution,[11] “deconvolution” of the difference function,[12] and “deconvolution” of the time-resolved fluorescence decay curves analyzed in planes parallel, $I_{\|}(t)$, and perpendicular, $I_{\perp}(t)$, to that of the polarized excitation pulse, respectively. The limitations of the latter two approaches, in analysis of the systems under investigation, are discussed. The relevance of the resultant polymer relaxation data is considered in the light of Kramers’[13] theory of particle translation over a potential energy barrier in the presence of frictional (collisional) resistance and the theories developed by Helfand et al.[14−16] to describe conformational changes in polymers.

Two excitation sources, a picosecond laser system and the Synchrotron Radiation Source (SRS), CLRC, Daresbury, have been used to generate the TRAMS data. The agreement between the polymer relaxation data obtained using the separate time-resolved spectrometers is excellent for both the PMMA and the PMA systems. This creates confidence both in the TRAMS approach and in the resultant relaxation information. It is concluded that the solvent, dichloromethane, exerts an influence over the polymer/relaxation characteristics which exceeds that which might be expected in the instance whereby the solvent serves merely to provide “frictional resistance” to the motion of either macromolecule. Our data may indicate that specific polymer/solvent and/or polymer/label interactions are involved. This observation is discussed with respect to recent studies of the dependence of local motions of macromolecules upon the viscosity of the medium in which they are dispersed.[17−19]

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Experimental Section

Materials. 1-Vinylnaphthalene (VN) was synthesized from methyl-1-naphthylcarbinol (Koch-Light) by dehydration with $KHSO_4$ (BDH). The monomer was purified by fractional distillation under reduced pressure (10^{-2} Torr) immediately prior to use. Acenaphthylene (ACE) (Aldrich) was recrystallized from ethanol and triply vacuum sublimed. Methyl methacrylate (Koch-Light) and methyl acrylate (Aldrich) were washed with 10% NaOH(aq) to remove inhibitor followed by H_2O until the washings were neutral. The monomers were dried over molecular sieves prior to prepolymerization with UV light followed by fractional distillation under high vacuum.

Polymers, PMMA and PMA, labeled with VN or ACE were prepared by free-radical bulk polymerization to low conversion (<5%), under high vacuum, using AIBN as initiator at 60 °C. The concentration of fluorescent comonomer was 0.5 mol %. The polymers were purified by precipitation from benzene into a 10-fold excess of cold methanol (−30 °C), and the mixture was allowed to warm to room temperature under constant agitation. The process was repeated several times.

Dichloromethane (BDH) was fractionally distilled before use and checked for purity using fluorescence spectroscopy. Solutions for time-resolved spectroscopy contained 0.1 wt % polymer.

Characterization. Molar masses of the labeled polymers were determined by size exclusion chromatography using polystyrene gel columns and THF as eluant. The samples are all high polymers, $10^5 < \bar{M}_n < 4 \times 10^5$ with $2.1 < \bar{M}_w/\bar{M}_n < 2.5$.

Instrumentation. TRAMS were performed on dilute dichloromethane solutions of the four labeled polymers using the technique of time-correlated single photon counting. Two sources, a laser and a synchrotron, were used for excitation. These sources have been described previously,[7,20−22] and only the briefest of details are given here.

The laser source consisted of a Spectra-Physics mode-locked, cavity-dumped and frequency-doubled dye laser, pumped synchronously by a mode-locked, Spectra-Physics Model 171 argon ion laser. The synchrotron was the SRS, Daresbury, U.K. In both spectrometers, Philips XP2020Q photomultipliers were used as detectors in collection of both time-resolved fluorescences and instrument response functions.

Results and Discussion

TRAMS involve observations of the time dependences of the intensities of luminescence emitted in planes parallel, $I_{||}(t)$, and perpendicular, $I_{\perp}(t)$, respectively, to that of the polarized incident radiation used to excite the sample. Typical data are shown in Figure 1 for an ACE-labeled sample of PMMA in dilute CH_2Cl_2 solution at 273 K. The major problem associated with such experiments, given that data of high resolution are collected, is the recovery, in a reliable fashion, of the rotational relaxational information embodied in the observed luminescence decay curves.

The time-dependent anisotropy function, $r(t)$, is related to the reorientational relaxation characteristics of the chromophore in a manner which is determined by the asymmetry of the motion of the luminescent molecule. In the case of labeled macromolecules, the rotational behavior of the reporter group will be dictated (if the label *is* to be a useful interrogator of the polymer dynamics) by the anisotropy of the motion of the kinetic unit to which the label is attached. In the case of a pseudospherical rotor, the emission anisotropy decays exponentially as in eq 1

$$r(t) = r_0 \exp(-t/\tau_c) \qquad (1)$$

where τ_c is the correlation time for the rotational reorientation of the label and r_0 is the intrinsic anisotropy.

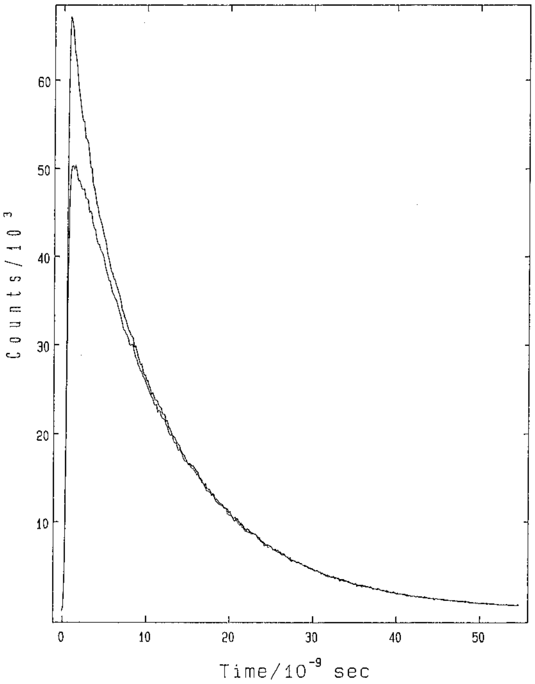

Figure 1. Temporal profiles of fluorescence from ACE-labeled PMMA in CH_2Cl_2 at 273 K, analyzed (at 340 nm) in planes parallel (upper curve) and perpendicular, respectively, to that of the pulsed, vertically polarized synchrotron radiation used for excitation (at 290 nm).

The observed emission anisotropy, $R(t)$, is constructed from $I_{||}(t)$ and $I_{\perp}(t)$ as in eq 2

$$R(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + 2I_{\perp}(t)} = \frac{D(t)}{S(t)} \qquad (2)$$

where $D(t)$ and $S(t)$ are the "difference" and "sum" functions, respectively. Since both $I_{||}(t)$ and $I_{\perp}(t)$ are distorted relative to their true decay profiles [($i_{||}(t)$ and $i_{\perp}(t)$, respectively] by the finite width of the instrument response function, $P(t)$ [the excitation pulse profile as observed *via* the timing components used in detection], $R(t)$ is also affected, and is not equivalent to $r(t)$. This can pose problems in retrieval of relaxation data since, unlike $I_{||}(t)$ and $I_{\perp}(t)$, $R(t)$ is not amenable to conventional reconvolution analysis [using $P(t)$] in modeling $r(t)$. Various approaches may be adopted in recovering polymer relaxation data from TRAMS. These have been discussed previously (see, for example, refs 5 and 7, and references therein) and will be discussed only briefly here.

(1) Direct Vector Reconvolution (DVR). In DVR, suitable functions are chosen to represent $i_{||}(t)$ and $i_{\perp}(t)$. These models are applied in reconvolution analyses with the measured "prompts", $P_{||}(t)$ and $P_{\perp}(t)$, to generate fits to $I_{||}(t)$ and $I_{\perp}(t)$, respectively, which are then optimized.

In the simplest case of a spherical rotor, for which $r(t)$ would be described by eq 2, $i_{||}(t)$ and $i_{\perp}(t)$ would be given by

$$i_{||}(t) = \exp(-t/\tau_f)[1 + 2r_0 \exp(-t/\tau_c)] \qquad (3)$$

$$i_{\perp}(t) = \exp(-t/\tau_f)[1 - r_0 \exp(-t/\tau_c)] \qquad (4)$$

provided the luminescence of the label is described adequately by a first-order decay law, characterized by a lifetime τ_f.

In principle, each of these model functions could be adopted in reconvolution analyses [to fit $I_{||}(t)$ and $I_{\perp}(t)$, respectively] leading to recovery of τ_c. In addition, the data sets $I_{||}(t)$ and $I_{\perp}(t)$ could, in principle, be combined in a global[23] analytical fitting procedure. In practice, however, difficulties can be encountered (even in instances wherein τ_f is constrained to equal that obtained in reconvolution analyses of fluorescence data collected under "magic angle" conditions, in order to facilitate convergence during fitting).[7]

Iterative reconvolution of $I_{||}(t)$ and $I_{\perp}(t)$, using the appropriate $P(t)$, produced, for the lower temperature, laser-generated data, statistically adequate fits ($\chi^2 \leq 1.3$; random distribution of residuals etc.) using dual exponential functions to model $i_{||}(t)$ and $i_{\perp}(t)$. Furthermore, fluorescence decays from both ACE and VN labels for both PMA and PMMA systems, analyzed under "magic angle" conditions, were adequately described by single exponential functions. This infers (through consideration of eqs 3 and 4) that the relaxation behavior of both PMMA/label and PMA/label systems achieves adequate representation by a simple first-order decay model for $r(t)$, as represented by eq 1: application of more complex models in description of the macromolecular dynamics of any of the polymer/label combinations is simply not justified in terms of the current data. However, recovery of τ_c values, characteristic of each label's rotational motion, is not without complication, as noted below.

For a given polymer, PMMA or PMA, reconvolution analyses of $I_{||}(t)$ and $I_{\perp}(t)$, using eqs 3 and 4, produced, at the lowest temperatures accessed (230 and 245 K), values of τ_c for each label which were in reasonable agreement. Furthermore, these estimates of τ_c were concordant (within experimental error) with those recovered from analyses of the corresponding difference function, $D(t)$ (see below). As temperature increased, estimates of τ_c, obtained by analysis of $I_{\perp}(t)$, for each of the polymer/label species not only deviated from those recovered from $I_{||}(t)$ and $D(t)$ but also showed fluctuations in their apparent temperature dependence. This was particularly evident for the rapidly relaxing PMA systems and results from the increasing uncertainty in recovery of small values of τ_c in dual exponential analyses of $I_{\perp}(t)$ (in particular).

These observations can be rationalized by consideration of the nature of $i_{\perp}(t)$ as depicted by eq 4. The amount of relaxation information inherent to $i_{\perp}(t)$ is less than that contained in $i_{||}(t)$ (*cf.* eq 3). Recovery, with accuracy, of a value of τ_c, which is relatively short compared to τ_f, places stringent demands upon the ability of dual exponential analyses [of both $I_{\perp}(t)$ and $I_{||}(t)$] to *resolve* the two decay parameters. For example, consider the PMMA/ACE system at 298 K: τ_f is 15.5 (±0.3 ns) as determined (±3 standard deviations) in single exponential analysis of the "magic angle" fluorescence decay curve. As discussed below, r_0 is *ca.* 0.13. Recovery of the value of τ_c (1.3 ns) produced in analysis of both $I_{||}(t)$ and $D(t)$ (see below) requires *reliable* estimation of a "lifetime" of 1.2 ns in a dual exponential analysis of either $I_{||}(t)$ or $I_{\perp}(t)$ in conjuction with that of 15.5 ns for τ_f. This clearly poses problems which are considerable in consideration of $I_{||}(t)$ data and insurmountable for $I_{\perp}(t)$. As noted above, the situation is worse for the PMA/label systems and for all systems at higher temperatures, since the anisotropy information constitutes a very small component of the overall, observed intensity profiles.

Table 1. Rotational Correlation Times (τ_c) for the Various Polymer/Label Systems Obtained by Combined Analyses of $I_{||}(t)$ and $D(t)$ Data [Values (and Associated Confidence Limits) Are in ns]

T/K	PMMA/ACE	PMMA/VN	PMA/ACE	PMA/VN
298	1.3 (±0.1)	1.3 (±0.2)	0.8 (±0.3)	0.5 (±0.1)
275	2.2 (±0.2)	2.2 (±0.5)	*a*	0.8 (±0.1)
260	3.2 (±0.5)	2.7 (±0.3)	1.3 (±0.2)	1.0 (±0.2)
245	4.5 (±0.7)	3.6 (±0.5)	1.8 (±0.3)	1.3 (±0.2)
230	5.6 (±0.7)	4.9 (±0.7)	2.5 (±0.3)	1.7 (±0.3)

[a] Despite repeated experiments at this temperature, analyses of $I_{||}(t)$ and $D(t)$ data would not "converge" to a common value of τ_c.

The arguments presented above are substantiated at higher temperatures in consideration of $I_{||}(t)$ and $I_{\perp}(t)$ data generated by use of synchrotron radiation for excitation. For no data set pairing [$I_{||}(t)$ and $I_{\perp}(t)$] could reasonable concordance between τ_c data be obtained in the higher temperature regime employed in the synchrotron experiments.

The limitations implicit in this form of data retrieval from $I_{||}(t)$ and $I_{\perp}(t)$ as separate observables also restrict global analysis of these conjunct data sets. Attempted global analyses (of both synchrotron and laser-generated fluorescences) produced inconsistent data sets (τ_f, τ_c) except at the very lowest temperatures accessed. [We have not used the global[23] approach as it *might* be applied: had we had confidence in the ability of these reconvolution procedures to retrieve τ_c data from $I_{||}(t)$ and $I_{\perp}(t)$, we would have collected sets of $I_{||}(t)$ and $I_{\perp}(t)$ responses at a variety of analysis wavelengths. This procedure, of undoubted virtue in other photophysical situations where the (two) decay parameters might be well resolved and in which wavelength variation would alter the relative contributions of the two components to the overall fluorescence, was not considered appropriate to the current study.]

(2) Analysis of Difference Curves, *D*(*t*). $D(t)$ (defined in eq 1) can be used[12] to generate relaxation data. Consideration of eqs 3 and 4 reveals that when the decays of both fluorescence and anisotropy are described by single exponential functions, the difference function, unperturbed by the excitation function, $d(t)$, is given by

$$d(t) = r_0 \exp[-(\lambda_f + \lambda_c)t] \qquad (5)$$

where $\lambda_f = \tau_f^{-1}$ and $\lambda_c = \tau_c^{-1}$.

Single exponential analyses of $D(t)$ data constructed from laser-generated fluorescence data produced, in the lower temperature region (230−298 K) examined, estimates of τ_c which were generally in good accord with those obtained in DVR analyses of the corresponding $I_{||}(t)$ data. Typical combined estimates of τ_c are listed, with associated "confidence limits", in Table 1.

Combined analyses of the laser-generated $I_{||}(t)$ and $D(t)$ data also allowed estimates of r_0 to be made for the various polymer/label combinations. In general, good agreement was obtained between these values (for a given label) and those generated (i) using the impulse reconvolution analytical approach (see below) and (ii) for other polymer/label/solvent systems (see, for example, refs 24−27). These concordances promote confidence in the ability of the DVR procedure and analysis of $D(t)$ to produce meaningful relaxation information from the laser-generated data in the lower temperature regime. This confidence is justified by the agreement found with the results furnished by the impulse recon-

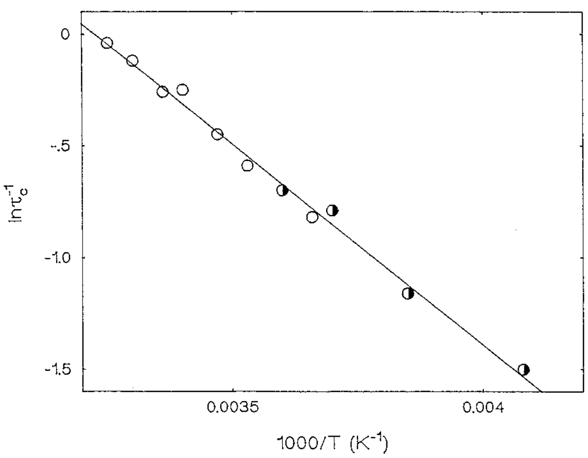

Figure 2. Arrhenius representation of the temperature-dependence of τ_c [*cf.* text, eq 1] for PMMA/ACE in CH_2Cl_2: (○) synchrotron data; (◑) laser data.

volution[9,10] and autoreconvolution[7,11] approaches, from synchrotron-generated data, as described below.

(3) Impulse Reconvolution (IR).[9,10] IR represents the most versatile and sophisticated approach to "deconvolution" of TRAMS data that has been developed to date.

Recoginizing that $r(t)$ is related to the true time responses, $d(t)$ and $s(t)$, of the difference and sum functions, respectively, *via*

$$r(t) = d(t)/s(t) \qquad (6)$$

the method uses a function providing a "best fit" to the observed $S(t)$ data. [The model function employed is of whatever complexity is required to produce an adequate representation of $S(t)$.] The resultant impulse response function $\{I_s(t)\}$ is combined with an appropriate mathematical model of $r(t)$ to fashion a "best fit" to $D(t)$. In so doing, the IR approach recognizes that the impulse response functions for $r(t)$, $s(t)$, and $d(t)$ are co-related *via*

$$\{I_r(t)\}\{I_s(t)\} = \{I_d(t)\} \qquad (7)$$

Typical relaxation data, recovered in IR analyses of PMMA/ACE fluorescence data covering a range of temperatures between 230 and 308 K and adopting a single exponential decay function to model $r(t)$ (*cf.* eq 1) are plotted, in Arrhenius form, in Figure 2. Excellent agreement between the data recovered from laser-generated fluorescences and those resultant upon use of the SRS for excitation is evident. In a similar manner, the TRAMS data for the other polymer/label combinations also achieved adequate description assuming a single exponential decay model for $r(t)$. Arrhenius plots for all four polymer/label systems studied are collated in Figure 3, and activation energy parameters, characteristic of the temperature dependence of τ_c, are listed in Table 2 and are discussed below.

(4) Autoreconvolution (AR).[7,11] The AR method relies upon the fact that, in its decay, $i_{||}(t)$ augments $i_{\perp}(t)$ in a manner akin to that of an excitation "prompt" promoting a fluorescence response: this relationship between $i_{||}(t)$ and $i_{\perp}(t)$ is similar to that adopted by the "monomer" decay in time-resolved studies of excimer formation or that of a donor species in energy transfer. The AR concept[11] is a particular example of the convolution kinetics[28-30] approach to data recovery from time-resolved emission experiments.

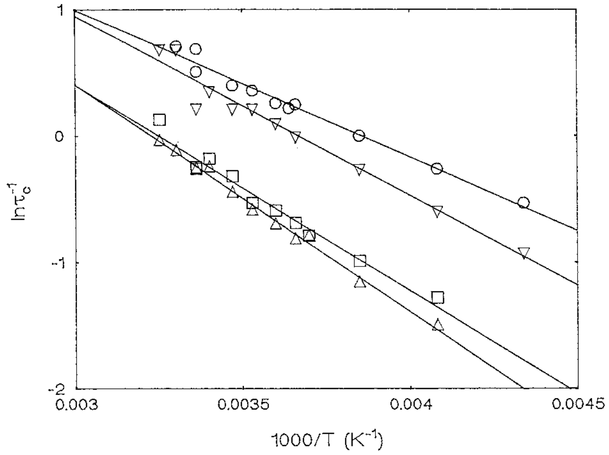

Figure 3. Arrhenius plots of segmental relaxation data for (△) PMMA/ACE, (□) PMMA/1-VN, (▽) PMA/ACE, and (○) PMA/1-VN.

Table 2. Activation Parameters for Intramolecular Segmental Relaxation of PMMA and PMA in CH_2Cl_2

polymer	label	E^*/(kJ mol^{-1})	E_s/(kJ mol^{-1})
PMMA	ACE	14.9	8.1
PMMA	VN	13.5	6.7
PMA	ACE	11.7	4.9
PMA	VN	9.6	2.8

In the AR approach, $I_{||}(t)$ is used to deconvolute $I_{\perp}(t)$ according to

$$I_{\perp}(t) = I_{||}(t) \otimes m(t) + \alpha I_{||}(t) \qquad (8)$$

where $m(t)$ is a model function, the form of which depends upon those of $i_{||}(t)$ and $i_{\perp}(t)$. Evaluation of the factor α allows r_0 to be estimated within this "deconvolution" procedure. AR is useful in that it provides an alternative means of recovery of relaxation data from anisotropy information for comparison with those afforded by IR analyses. Furthermore, it provides a rigorous procedure whereby the applicability of the function adopted in modeling the anisotropy may be tested.

When $i_{||}(t)$ and $i_{\perp}(t)$ are described by eqs 3 and 4, $m(t)$ will assume the form of a single exponential decay function. AR analyses of all data sets revealed that reconvolutions using a single exponential function for $m(t)$ in combination with $I_{||}(t)$, according to eq 8, provided statistically adequate fits to $I_{\perp}(t)$ as judged, for example, by the distribution of residuals, etc. This, in turn, confirms the conclusion, drawn from the results of the other reconvolution procedures and discussed above, that $r(t)$ for each of the polymer/label systems in CH_2Cl_2 is well characterized by eq 1 in the temperature range 230−310 K. In each case, good agreement was achieved between the values of τ_c obtained by AR analysis and those resultant upon the IR approach.

Temperature Dependence of Intramolecular Segmental Relaxation of PMMA and PMA in CH_2Cl_2. As revealed in Figure 3, the parameter, τ_c^{-1}, characteristic of the rate of chromophore reorientation in the PMMA/ACE and PMMA/VN systems is, for dilute solutions in CH_2Cl_2, described well by an Arrhenius-type temperature dependence, over the limited (80 K) temperature range assessed in this study. Within such a format,

$$\ln(\tau_c^{-1}) = A \exp(-E^*/RT) \qquad (9)$$

wherein E^* is the "activation energy" for rotational

Table 3. Literature Values of Activation Parameters for Intramolecular Segmental Motions of PMMA and PMA in Dilute Fluid Solutions

polymer	solvent	technique	E^*/ (kJ mol^{-1})	E_s/ (kJ mol^{-1})
PMMA	toluene[32]	DR[a]	27	18.3
PMMA	toluene[33]	ESR	20	11.3
PMMA	toluene[34]	TRAMS	21	12.3
PMMA	ethyl acetate[35]	ESR	33 (<303 K)[b]	25.2
			22 (>303 K)[b]	14.2
PMMA	dibutyl phthalate[35]	ESR	60	*ca.* 35
s[c]-PMMA	benzene[36]	TRAMS	10.5	0
s[c]-PMMA	$CHCl_3$[36]	TRAMS	10	2.5
PMA	toluene[32]	DR[a]	23	14.3
PMA	toluene[33]	ESR	19	10.3
PMA	toluene[34]	TRAMS	23	14.3

[a] DR = dielectric relaxation. [b] PMMA is reported[37] to undergo a conformational transition in ethyl acetate, which is detected at 303 K[35] in the ESR experiment. [c] Syndiotactic PMMA.

randomization of the photoselected distribution of chromophores. If the polymer/label combination is such that the motion of the chromophore reliably reflects that of the host segment of the polymer chain to which it is affixed, E^* will represent the "activation energy" for intramolecular segmental motion of the polymer in the solvent concerned.

Reference to Table 2 shows that there is a reasonable agreement between the values of E^* for a given polymer (PMMA or PMA) which are obtained using ACE or VN copolymerized residues as fluorescent label. However, although the values of E^* agree within the errors of the current experiments (*ca.* ±1.5 kJ mol^{-1}) those of the VN-labeled systems are lower than those of their ACE analogs in both cases. Such an observation might be anticipated considering the potential for the VN chromophore to rotate independent of its polymeric host, should the motions of substituent and macromolecular backbone fail to attain cooperativity. (There is published evidence[27] of enhanced depolarization of the fluorescence of the VN label, relative to that of ACE, albeit in more constrained environments than those encountered in this study. There is little doubt that in the considerably restricted conditions evident in the polymeric solid state, the VN label, as revealed by phosphorescence anisotropy,[31] can achieve independence of motion from that of the polymer segments.) Given that E^* (particularly that for the ACE-labeled systems) reflects, in a reliable manner, the relaxation characteristics of each polymer system, we can discuss the ways in which the current data compare with expectation, both on the basis of previous studies and from theoretical approaches to the relaxation characteristics of polymer chains.

Table 3 lists the values of E^* which have been reported for PMMA and PMA in a variety of solvents using the techniques of dielectric relaxation,[32] ESR spectroscopy,[33,35] and TRAMS.[34,36] It is apparent that there is little correlation between these estimates of E^* and those of the current work. This is not entirely unexpected, however, since the polymer dynamics will be affected by the nature of the solvent and the frictional resistance to motion that it generates. A common practice in dealing with solvent effects upon macromolecular dynamics is to consider Kramers' [13] approach to passage of a particle over a potential energy barrier in the presence of frictional resistance in conjunction with the application by Helfand et al.[14−16] of this theory to the local motions of polymers.

In the high-friction limit, τ_c for rotational diffusion of a polymer segment is given by

$$\tau_c = B\eta \exp(E_s/RT) \tag{10}$$

where B is a constant. Comparison with eq 9 shows that the activation energy, E_s, associated with rotational motion over a potential energy barrier is related to E^* by

$$E_s = E^* - E_\eta \tag{11}$$

where E_η is the activation parameter associated with solvent flow. The resultant values of E_s are listed in Table 2 for the labeled polymers studied in this work and in Table 3 for PMMA and PMA as studied in other solvents using various relaxation techniques. Far from being constant, there is a wide variation between the estimates of E_s. Provided that the various techniques sense the same local motions of the polymer chains, the differences between the values for the apparent intrinsic barriers to internal rotation of the macromolecules are disconcerting.

Recently, Ediger et al.[17−19,38] have reported that the local dynamics of both polyisoprene and polystyrene do not exhibit the linear dependence upon viscosity suggested by eq 9. Adopting an approach similar to that of Fleming et al.[39−42] in studies of isomerization of small molecules in solution, it was argued[17−19] that

$$\tau_c = C\eta^\alpha \exp(E_s/RT) \tag{12}$$

wherein C is a constant and $0 < \alpha < 1$. Within this framework, the power dependence of τ_c upon viscosity is accommodated within eq 13 as

$$E_s = E^* - \alpha E_\eta \tag{13}$$

Clearly, establishment of the power law governing the viscosity dependence of τ_c requires that E^* be obtained for more than one polymer/solvent system, for any given polymer. In addition, specific polymer−solvent interactions must be absent if the functional form of eq 12 is to apply, in general.

With the limited range of PMMA/solvent and PMA/solvent data sets available in Tables 2 and 3, it is not possible to obtain meaningful estimates of α and thence E_s. This is not solely a consequence of the relatively large error limits (*ca.* ±10−20%) associated with the various estimates of E^* collated here: it would appear that specific interactions might be apparent between PMMA or PMA and CH_2Cl_2 and, indeed, other solvents within the limited range presented here. Establishment of this point will require a much more extensive study of the effects of solvent and temperature upon the local dynamics of polyacrylates and/or polymethacrylates than has been hitherto attempted. Ideally, studies of the type undertaken by Ediger et al.[17−19] on polyisoprene or polystyrene, covering significant ranges of solvents, should be undertaken if the roles of solvent viscosity and specific polymer interactions in determining the chain dynamics of acrylic systems are to be clarified.

Conclusions

1. Intramolecular segmental relaxation processes in PMMA and PMA in dichloromethane as solvent and revealed in the time-resolved anisotropies of the covalently bound naphthyl labels, ACE and VN, are described adequately by first-order decay laws.

2. The resultant rate parameters exhibit an Arrhenius temperature dependence over the temperature

range 230−310 K. The resultant apparent activation energies, E^*, for the intramacromolecular dynamics in dichloromethane solution are *ca*. 14.2 (±1.5) and 10.7 (±1.5) kJ mol^{-1} for PMMA and PMA, respectively. These values are considerably lower, in each case, than those obtained for the same polymer in other solvents using a variety of relaxation techniques.[32−36]

3. The differences apparent in E^* for PMMA or PMA dissolved, for example, in toluene and those obtained for dichloromethane solutions cannot be rationalized in terms of differences in the temperature dependences of the solvents' macroscopic viscosities if it is assumed that the solvents merely act to provide a frictional resistance to segmental motion. It is tentatively suggested that both PMMA and PMA exhibited specific interactions with the dichloromethane and/or other solvents. Alternatively, it may be that the dichloromethane associates specifically with the naphthyl labels used in this study, perturbing the relaxation processes that we wish to investigate.

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