

Experimental Section

Materials.

In principle, each of these model functions could be adopted in reconvolution analyses [to fit $I_{\parallel}(t)$ and $I_{\perp}(t)$, respectively] leading to recovery of $\hat{\omega}_c$. In addition, the data sets $I_{\parallel}(t)$ and $I_{\perp}(t)$ could, in principle, be combined in a global²³ analytical fitting procedure. In practice, however, difficulties can be encountered (even in instances wherein $\hat{\omega}_r$ 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 $I_{\parallel}(t)$ and $I_{\perp}(t)$, using the appropriate $P(t)$, produced, for the lower temperature, laser-generated data, statistically adequate fits ($R^2 \in 1.3$; random distribution of residuals etc.) using dual exponential functions to model $i_{\parallel}(t)$ 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 $\hat{\omega}_c$ 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 $I_{\parallel}(t)$ and $I_{\perp}(t)$, using eqs 3 and 4, produced, at the lowest temperatures accessed (230 and 245 K), values of $\hat{\omega}_c$ for each label which were in reasonable agreement. Furthermore, these estimates of $\hat{\omega}_c$ were concordant (within experimental error) with those recovered from analyses of the corresponding difference function, $D(t)$ (see below). As temperature increased, estimates of $\hat{\omega}_c$, obtained by analysis of $I_{\perp}(t)$, for each of the polymer/label species not only deviated from those recovered from $I_{\parallel}(t)$ 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 $\hat{\omega}_c$ 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

volution^{9,10} and autoreconvolution^{7,11} approaches, from synchrotron-generated data, as described below.

(3) Impulse Reconvolution (IR).^{9,10} IR represents

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 evidence²⁷ 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)

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