Quantitative Determination of the Radius of Gyration of Poly(methyl methacrylate) in the Amorphous Solid State by Time-Resolved Fluorescence Depolarization Measurements of Excitation Transport

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ABSTRACT: Excitation transport among naphthyl chromophores in low concentration on isolated coils of poly(2-vinylnaphthalene-co-methyl methacrylate) in a poly(methyl methacrylate) host is monitored by time-resolved fluorescence depolarization spectroscopy. Comparison of the experimental results to a recently developed theory for excitation transport in finite volume systems employing Gaussian segmental distribution functions allows the quantitative evaluation of the copolymer root-mean-square radius of gyration \((R_g)^{1/2}\). The dependence of \((R_g)^{1/2}\) on the polymer is determined for three 23000 \(M_w\) copolymers containing 9%, 6%, and 4% 2-VN. The measured \((R_g)^{1/2}\) are independent of 2-VN concentration. The \((R_g)^{1/2}\) values for the 23000 \(M_w\) copolymers and a 80000 \(M_w\) 9% 2-VN copolymer are identical with literature \((R_g)^{1/2}\) determinations for the same molecular weight PMMA polymers in \(\theta\)-solvents. The results demonstrate the quantitative utility of electronic excitation transport monitored by fluorescence depolarization spectroscopy as a tool for the determination of polymer conformation in the solid state.

I. Introduction

The macroscopic properties of solid-state polymer systems arise from the microscopic interaction of the individual polymer chains. The bulk properties of polymer blends are critically dependent on the mixing of blend components on a molecular level. Through the careful adjustment of the composition of blends technological advances in the engineering of polymer materials have been made. In order to understand these systems more fully, it is desirable to investigate the interactions of individual polymer chains with the host environment. A polymer coil in a solid blend can adopt a large number of configurations. The probability of any coil conformation depends on the thermodynamic interaction of the coil with its environment, on the geometric requirements of the allowed bond angles and rotations, and on the associated conformational entropy. A change in the thermodynamic properties of the environment will lead to a change in the average chain conformation. A very sensitive indication of these thermodynamic interactions is the root-mean-square radius of gyration of a guest polymer dispersed in a polymer host matrix.

Currently, neutron scattering is the most common method used to determine \((R_g)^{1/2}\) of isolated polymer coils in the solid state. This technique has proven to be quite informative, and although it has the advantage of providing a direct probe of chain structure, its use suffers from a number of limitations. A monochromatic neutron source is required. In order to produce contrast, the polymer component being investigated, or the polymer host, must be deuterated. The mechanical and thermodynamic properties of a number of polymers and polymer blends are strongly affected by deuteriation. It is difficult or impossible to assess the effect of deuteriation on neutron scattering measurements on polymer blends. Thus, conclusions drawn from the deuterated systems do not rigorously apply to the hydrogenated blends. Finally, scattering from the host makes it difficult to investigate the behavior of the guest polymer at very low concentration (<1%). Many polymer blends undergo phase separation at even lower concentrations. For these systems in particular, neutron scattering is incapable of providing structural and thermodynamic properties of the isolated guest coil. The limitations of neutron scattering have created an interest in the use of excitation transport techniques to study the properties of solid-state polymer systems.

The dependence of excitation transport on local chromophore concentration has been used to provide qualitative information on the characteristics of polymers in blends. Excimer fluorescence resulting from excitation transport has been employed to characterize polymer miscibility, phase separation, and the kinetics of spinodal decomposition. Qualitative characterization of phase separation in blends has also been investigated through transport with trapping experiments. In these experiments one polymer in the blend contains donor chromophores and the second contains acceptors. Selective excitation of the former and detection of the latter provide a qualitative measure of interpenetration of the two components.

Electronic excitation transport is very sensitive to the separation and orientation of chromophores. Techniques that monitor the rate of excitation transport among chromophores on a polymer chain are direct probes of the conformation. Recent experiments measuring fluorescence depolarization arising from excitation transport among chromophores on isolated guest coils in solid-state polymer blends demonstrated the feasibility of determining the relative size of individual chains in various host environments. As a consequence of the excellent signal-to-noise ratio achievable in optical experiments, excitation transport can be employed to investigate a minor component in a blend at concentrations several orders of magnitude smaller than is possible with neutron scattering techniques. This allows the study of isolated coils in both miscible blends and immiscible blends, which tend to phase separate at very low concentrations. It is easy to understand, qualitatively, the relationship between the dynamics of excitation transport among chromophores randomly tagged in low concentration on an isolated polymer coil and the size of the coil. An ensemble of tagged coils in a polymer blend will have some ensemble-averaged root-mean-square radius of gyration, \((R_g)^{1/2}\). If the thermodynamic interaction between the guest coils and the host is very favorable, \((R_g)^{1/2}\) will be large and the average distance between chromophores will be large. Since the rate of excitation transport depends
on 1/\sigma^2, where \sigma is the chromophore separation, transport will be slow. If the same guest polymer is placed in a different host, in which the guest–host thermodynamic interactions are less favorable, the coils will contract in order to minimize guest–host interactions.\textsuperscript{2} The average chromophore separation will decrease. This decrease leads to more rapid excitation transport. The 1/\sigma^2 rate dependence makes excitation transport observables very sensitive to small changes in \langle R_2^2 \rangle^{1/2}. A more detailed description of the relationship between \langle R_2^2 \rangle^{1/2} and the experimental observables is given in section II.

In a manner somewhat analogous to the effect of deuteration on a neutron scattering experiment, it is likely that attachment of the chromophores labels necessary for excitation transport experiments will cause perturbations to the polymer chain conformation. However, as experimentally demonstrated in detail below, it is possible to assess the extent, if any, of such perturbations and change the amount of label present to either eliminate the effects or permit an extrapolation to zero chromophore concentration. This is not possible for the deuteration that is necessary in neutron scattering experiments.

In section IV we present the results of time-resolved fluorescence depolarization experiments that monitor the rate of donor-to-donor excitation transport on copolymers of methyl methacrylate and 2-vinyl naphthalene dispersed in a host matrix of poly(methyl methacrylate) (PMMA). The composition of the blends was such that the copolymer coils were isolated in the host. We studied copolymers at two different molecular weights. The experimental results were analyzed with a recently developed theory, which relates the rate of excitation transport to the coil size, and provide quantitative measurement of \langle R_2^2 \rangle^{1/2} for the guest copolymers.\textsuperscript{3} The mole percent of naphthalene groups on the copolymers is low, and the effect on the chain conformation is small. The \langle R_2^2 \rangle^{1/2} determined here agree well with values obtained for PMMA by light scattering in \Theta-solvents. However, to ensure that there is no significant effect due to the presence of the naphthalene groups, experiments were performed on a series of copolymers of the same molecular weight but varying in the number of naphthalenes per polymer chain. The results demonstrate that the copolymer size is independent of the number of naphthalenes per coil for relatively low naphthalene concentrations.

II. Relation of Experimental Observables and Theory

In systems involving donor–donor excited–state transport, the fundamental quantity of theoretical and experimental interest is \( G(t) \), the ensemble-averaged probability that an originally excited chromophore is excited at time \( t \).\textsuperscript{7} \( G(t) \) contains contributions from excitations that never leave the originally excited chromophore and from excitations that return to the initially excited chromophores after one or more transfer events. \( G(t) \) does not contain loss of excitation due to lifetime (fluorescence) events. In this section we discuss how \( G(t) \) can be obtained experimentally from time-resolved fluorescence depolarization data. The method used to calculate the theoretical \( G(t) \) and its relationship to \( \langle R_2^2 \rangle^{1/2} \) is briefly described.

If a sample of randomly oriented chromophores is excited by a short pulse of plane polarized light, the decay of the fluorescence intensities polarized parallel \( (I_i(t)) \) and perpendicular \( (I_p(t)) \) to the exciting light can be written as

\[
I_i(t) = e^{-\tau t / (1 + 2\sigma^2(t))} \quad I_p(t) = e^{-\tau t / (1 - \sigma^2(t))}
\]

\( \tau \) is the fluorescence lifetime, and \( \sigma(t) \) is the fluorescence anisotropy. \( \sigma(t) \) contains information about all sources of depolarization. If the transition dipoles of the chromophores in a solid polymer matrix are randomly oriented, the main source of depolarization in these experiments is excitation transport. The initially excited ensemble is polarized along the direction of the excitation \( E \) field and gives rise to polarized fluorescence. Transport occurs into an ensemble of chromophores with randomly distributed dipole directions, and the fluorescence becomes unpolarized. The random distribution is assured by the low concentration of the chromophores. To a slight extent, on the time scale of interest, depolarization also occurs as a result of chromophore motion. In this case the fluorescence anisotropy is approximately

\[
\sigma(t) = C \Phi(t) G(t)
\]

where \( \Phi(t) \) is the rotational correlation function which contains the effects due to motion of the chromophores. \( C \) is a time-independent constant that describes the degree of polarization of the excitation and emission transitions involved. There are two approximations in eq 2. The first is that the rotational and energy transport contributions to depolarization are independent. This is an excellent approximation for the very slow and small extent of rotational depolarization in polymer blends on the time scale of interest. The second approximation is that \( G(t) \) decays to zero, resulting in complete depolarization; i.e., the irreversible transfer of excitation from the initially excited donor into the ensemble of unexcited donors results in total loss of polarization. For coils with a low concentration of randomly placed chromophores this is approximately true. The residual polarization is only 4%, which results in an insignificant error.\textsuperscript{10}

In order to obtain \( G(t) \) for a given polymer, experiments on two different samples must be performed. These samples differ only in that the guest copolymers have a different fraction of chromophore-containing monomers. Copolymer A is the polymer of interest and has an appreciable number of chromophores, such that excitation transport will occur. Its fluorescence anisotropy, \( \sigma(A) \), is given by eq 2. Copolymer B has such a small number of chromophores that excitation transport is negligible \( (\sigma(B) = 1) \) and only chromophore motion contributes to the anisotropy

\[
\sigma_B(t) = C \Phi(t) G_B(t)
\]

\( G_B(t) \) arising from the excitation transport on copolymer A can be calculated from the two experimental anisotropies:

\[
G(t) = r_A(t) / r_B(t)
\]

This method of determining \( G(t) \) has the advantage that detailed knowledge of the parameters \( C \) and \( \Phi(t) \) is unnecessary. \( r(t) \) for either copolymer can be obtained from the individual parallel and perpendicular components of the fluorescence intensity. From eq 1

\[
r(t) = \frac{I_i(t) - I_p(t)}{I_i(t) + 2I_p(t)}
\]

To obtain a value for \( \langle R_2^2 \rangle^{1/2} \) of copolymer A, we compare the experimentally determined \( G(t) \) to a theoretical calculation of \( G(t) \) for the same copolymer. Once the molecular weight and number of chromophores are known (these can be independently determined), the theory has only one adjustable parameter. This parameter is directly related to \( \langle R_g^2 \rangle^{1/2} \).

The theory employed to analyze the data presented here has been described in detail elsewhere.\textsuperscript{9} Only a brief
The theory we employ to describe the methods have been applied to infinite length polymer. The expansion was used to obtain an accurate approximation for the excited chromophore located at position \( i \). \( G_i(t) \) was then averaged exactly over all possible initial positions \( i \) to yield an approximation for the experimental observable \( G_i(t) \). While \( G_i(t) \) is approximate, no additional approximations are involved in obtaining \( G_i(t) \).

The first-order cumulant expansion has been applied to several problems besides chromophores randomly distributed in an infinite three-dimensional system. The problem of chromophores randomly distributed on a finite stack of planes has been treated recently. In this problem the excitation transport dynamics depend on which plane contains the initially excited chromophore. The first-order cumulant expansion was used to obtain an approximate expression for \( G_i(t) \), where \( i \) is the label of the plane containing the initial excitation. The observable \( G_i(t) \) is then found by averaging over the initial excitation conditions. This involves a sum over \( i \). As in the sphere problem described above, \( G_i(t) \) is approximate, but for the physical model considered, the average over \( i \) is performed exactly. The cumulant expansion was also used to reexamine the finite sphere problem. The investigators chose to approximate \( G_i(t) \) rather than \( G_i(t) \) by the cumulant expansion. Unlike the original treatment of the sphere problem, this approach approximates the average over the position of the initial excitation.

The problem of excitation transport among chromophores randomly tagged in low concentration on a finite length polymer coil is also a finite volume problem. Initial excitation of a chromophore near an end of the chain results in dynamics different from that of excitation of a chromophore near the middle of the chain because of the distinct distributions of chromophores about these two points. Peterson and Fayer have applied the first-order cumulant expansion to this problem. The details of the calculations and demonstrations of its accuracy are reported in ref 8. These investigators chose to apply the cumulant expansion to \( G_i(t) \), and then, within the context of the freely jointed chain model, they perform the average over the position of initial excitation exactly. This results in a more accurate approximation than applying the cumulant expansion to \( G_i(t) \) directly, since it avoids the approximate average over the initial location of excitation.

Using the chromophore distribution function, \( P_i(r_{12}) \), performing the cumulant expansion, and then averaging over the possible positions of the initially excited chromophore, we obtained an expression for \( G_i(t) \):

\[
G_i(t) = \frac{1}{N} \sum_{i=1}^{N} \exp \left[ \frac{4\pi}{2} \int_0^{\infty} \left( 1 - e^{-2\pi r_{12}^2} \right) P_i(r_{12}) r_{12}^2 \, dr_{12} \right]
\]

where \( \omega_{12} \) is the rate of excitation transport between two chromophores at a separation of \( r_{12} \). In eq 8, the exponential term is \( G_i(t) \) and the sum over \( i \) (chain segments) is the average over the initial positions of excitation.

For rapidly rotating chromophores \( \omega_{12} \) is given by:

\[
\omega_{12} = \left( \frac{R_0}{r_{12}} \right)^6 / \tau
\]

where \( \tau \) is the fluorescence lifetime and \( R_0 \) is the critical transfer radius. Equation 9 is the orientation-averaged expression for dipole–dipole interactions and is applicable to dynamic systems (e.g., chromophores in solution). For the experiments in this paper, the chromophores are essentially static, and \( R_0 \) in eq 9 must be replaced by:

\[
R_0' = (\gamma_2)^{1/2} R_0
\]

where \( \gamma_2 = 0.8468 \). Provided the molecular weight of the copolymer is known, eq 8 has only one adjustable parameter, the statistical segment length \( a \). This is directly related to \( R_g \) by:

\[
R_g = \frac{1}{2}(N a^2)
\]
to a theoretically calculated \( G(t) \) determined by adjusting the statistical segment length will give a measure of \( (R_g^2)^{1/2} \) for the copolymer.

### III. Experimental Section

#### A. Polymer Materials

Five copolymers of methyl methacrylate (MMA) and 2-vinyl-naphthalene (2-VN) were used in the fluorescence depolarization experiments. All were polymerized in benzene at 60 °C under nitrogen following the procedure of Fox et al.\(^\text{19}\). AIBN and butylthiol were used as initiator and chain-transfer reagent, respectively. The MMA (Aldrich) was washed with 5% NaOH, dried over NaSO\(_4\), and vacuum distilled. The 2-VN (Aldrich) was recrystallized from ethanol and sublimed once. The AIBN was recrystallized from ethyl acetate. The copolymers were recovered from the reaction mixture by precipitation into methanol and subsequently washed several times with cold methanol.

The desired molecular weight fractions were obtained from the resulting polydisperse copolymers by size exclusion chromatography using Sephacryl S-200 resin and THF as eluent. The GPC instrument was calibrated by using nearly monodisperse PMMA standards (Pressure Chemical, \( M_n/M_w < 1.1 \)). The copolymer used to determine the depolarization due to chromophore motion (0.0015 mol fraction 2-VN) was not fractionated. Its average molecular weight was determined by viscosity measurements. The mole fractions of vinyl-naphthalene monomer units in the copolymers were determined by absorption spectroscopy at 320 nm (Cary 17 spectrometer), based on a molar extinction coefficient of 400 mol cm\(^{-1}\) L\(^{-1}\) for ethyl-naphthalene. Table I gives a summary of the characteristics for the five copolymers.

The host polymer for all the blends was PMMA (Polysciences no. 4553, number-average molecular weight \( \sim 120,000 \)).

#### B. Sample Preparation

All samples were solid blends of the desired guest copolymer and the host PMMA prepared by melting in a stainless steel piston above the glass transition temperature. The procedure is the same as described previously.\(^\text{17}\) The samples were optically clear with no significant birefringence along the direction in which the pressure was applied. This was checked by viewing the samples through a polarizing microscope.

#### C. Data Acquisition

Figure 1 shows the experimental apparatus. The frequency-doubled (532 nm) output of an acousto-optically mode-locked, Q-switched Nd:YAG laser was used to synchronously pump a dye laser. The dye laser was cavity dumped with a Pockels cell to produce a single pulse at 640 nm, which was then frequency-doubled to give the -25 ps excitation pulse with a Pockels cell to produce a single pulse at 640 nm, which was then frequency-doubled to give the -25 ps excitation pulse. The frequency-doubled (532 nm) output of an acousto-optically mode-locked, Q-switched Nd:YAG laser is frequency-doubled and synchronously pumps a dye laser. The dye laser output is doubled to 320 nm for excitation. The polarization of the excitation beam is controlled by a half-wave plate. The fluorescence from the sample is collected by a fiber passed through a polarizer and a monochromator, and detected by a multichannel plate coupled to a transient waveform recorder. See text for further details. The fluorescence decays and average many decays to improve signal-to-noise ratios. The time resolution of the detection system was 1.0 ns.

If \( I_1(t) \) and \( I_2(t) \) were measured by rotating the polarization of the excitation pulse with a half-wave plate and keeping the detector polarization unchanged at vertical polarization. Since the detection efficiency of the monochromator and microchannel plate can very with the polarization of the light, this method ensures that the absolute ratio of \( I_1(t) \) to \( I_2(t) \) is preserved. For a typical sample, 100 fluorescence decays at a given excitation polarization were collected and added by the computer. The excitation polarization was then rotated, and an additional 100 decays were collected, added, and stored separately by the computer. This sequence was repeated and the additional data were added to the previously collected decays of the appropriate polarization until a total of 1000 decays at each polarization were collected. By use of eq 5, \( r(t) \) is then calculated for this set of decays. The entire sequence was repeated for the same spot and different spots on the same sample. No substantial or systematic differences were observed. The \( r(t) \) curves calculated from these separate data sets were then averaged together. Switching frequently between collecting fluorescence at the two polarizations minimizes any possible artifacts.

In addition to checking the birefringence of the samples in a polarizing microscope, the birefringence of the spot actually excited by the laser beam was checked by placing a polarizer and phototube in the excitation beam after the sample and measuring the ratio of the transmitted light parallel and perpendicular to the incident polarization. This ratio was 206±1 or higher for all samples and is large enough to ensure that there is no distortion in the data due to birefringence in the samples. Fluorescence data were also collected on samples of pure PMMA host material. The fluorescence from these samples was negligible compared to the fluorescence from the copolymer-containing samples.

#### D. Data Analysis

The experimental \( r(t) \) and \( G(t) \) were obtained from \( I_1(t) \) and \( I_2(t) \) by the point-by-point calculations of eq 4 and 5. For an accurate comparison of the experimental curves with theoretical \( G(t) \) curves calculated from eq 6–10, the

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**Table I: Copolymer Characteristics**

<table>
<thead>
<tr>
<th>copolymer</th>
<th>2-VN mole fraction</th>
<th>mol wt</th>
<th>( M_n/M_w )</th>
<th>chromophores/chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0015</td>
<td>50000</td>
<td>~2.5</td>
<td>1</td>
</tr>
<tr>
<td>4-23</td>
<td>0.0040</td>
<td>22700</td>
<td>9 ± 1</td>
<td>1</td>
</tr>
<tr>
<td>6-22</td>
<td>0.0069</td>
<td>22430</td>
<td>9 ± 1</td>
<td>1</td>
</tr>
<tr>
<td>9-23</td>
<td>0.0087</td>
<td>23400</td>
<td>20 ± 1</td>
<td>1</td>
</tr>
<tr>
<td>2-90</td>
<td>0.0087</td>
<td>59800</td>
<td>49 ± 2</td>
<td>1</td>
</tr>
</tbody>
</table>
We determined that the copolymer coils were
wt
plicability of the theory relating
guest copolymers are necessary to show the general ap-
the average number of naphthalenes on the chains.

Polymer coils were isolated in PMMA at this concentra-
3/8
sly~~ to be 13.0
osly~~ function of
theoretical expressions for
into the apparatus
response function. For this system the response function is well
approximated as Gaussian with fwhm = 1 ns. The theoretical
response function is then calculated from these new
II(t)
and
Il(t)
curves with eq 4 and 5.

For the theory described in section II, \( \langle R_e^2 \rangle^{1/2} \) is a linear
function of \( R_o \), \( R_o \) for the naphthalene chromophores on the
copolymer chains dispersed in PMMA was determined previ-
ously to be \( 13.0 \pm 0.6 \) A. This is the orientation-averaged \( R_o \)
which must be modified for the solid state as described in section
II.

IV. Results and Discussion

Earlier experiments have shown the utility of excitation
transport measurements in providing relative information
regarding coil size in polymer blends. The results of the
experiments described here demonstrate that monitoring
excitation transport on isolated coils in solid blends
through time-resolved fluorescence depolarization tech-
niques provides a quantitative measure of \( \langle R_e^2 \rangle^{1/2} \) for the
guest polymer. Experiments on different molecular weight
guest copolymers are necessary to show the general
applicability of the theory relating \( G(t) \) to \( \langle R_e^2 \rangle^{1/2} \) and to
confirm the utility of assuming a Gaussian segment dis-
tribution for PMMA. Since the presence of the naph-
thalene groups could perturb the average chain confor-
mation, \( \langle R_e^2 \rangle^{1/2} \) was determined for a series of copolymers
of essentially the same molecular weight but differing in
the average number of naphthalenes on the chains.

A. Determination of \( \langle R_e^2 \rangle^{1/2} \) for Copolymers of
Different Molecular Weights. Time-resolved fluores-
cence depolarization experiments were performed on
samples made from copolymer 9-23 (0.087 mol fraction 2-VN, 23400 \( M_w \)) and from copolymer 9-60 (0.087 mol fraction 2-VN, 59800 \( M_w \)) in 120000 \( M_w \) PMMA. In both
cases, the amount of copolymer in the host PMMA was
3/8 wt %. It has been determined previously that for a
20000 \( M_w \) copolymer of this type, this individual
copolymer coils were isolated in PMMA at this concen-
tration. We determined that the copolymer 9-60 coils were
also isolated at this concentration since a sample with 1/8
wt % of this copolymer gives the same anisotropy decay
as a sample with 3/8 wt % of the copolymer.

Figure 2 shows the polarized fluorescence decays (\( I_{||}(t) \)
and \( I_{\perp}(t) \)) for the copolymer 9-23/PMMA blend. Figure
3 (lower curve) shows the fluorescence anisotropy, \( r(t) \),
calculated from the data by using eq 5. Also shown (upper
curve) is \( r(t) \) obtained in the same manner for the 0.0015
mol fraction 2-VN copolymer (copolymer I in Table I).
The sample consists of 12% by weight of copolymer I.
This sample contains so few chromophores that depolar-
ization occurs solely as a result of chromophore motion.
There is no excitation transport.

As discussed in section II, to obtain the experimental
\( G(t) \) for copolymer 9-23, it is necessary to take the ratio
of the anisotropies of copolymer 9-23 to copolymer I. The
resulting experimental \( G(t) \) curve is shown in Figure 4.
Figure 5 shows the experimental \( G(t) \) obtained in the same
manner for copolymer 9-60. In both these figures, we also
show the best fits (smooth curves) obtained from the
theory described in section II. Variation of the single
adjustable parameter, the statistical segment length \( \alpha \),
results in \( \langle R_e^2 \rangle^{1/2} \) of 37 \pm 3 and 61 \pm 3 Å for the 23400
and 59800 \( M_w \) copolymers, respectively. The sensitivity
of the technique is demonstrated by theoretical curves at
\pm 2 Å from the best fits.

The measured \( \langle R_e^2 \rangle^{1/2} \) for these two polymers varies
with the square root of the chain length. This is as
expected for flexible coils and indicates that the Gaussian
segment distribution function utilized in the analysis of
the data is applicable to these copolymers. Neutron
scattering experiments on isolated PMMA coils in a deu-
teriated PMMA host show this same scaling of \( \langle R_e^2 \rangle^{1/2} \)
with molecular weight. Since these blends are essentially PMMA in PMMA, the
copolymers are approximately in \( \Theta \)-conditions. The effect of the naphthalene groups is discussed below.) True
\( \Theta \)-conditions for a solid blend would be PMMA in a
PMMA host of the same molecular weight. We do not expect that a host \( M_w \) of 120000 results in a significant
deviation from \( \Theta \)-conditions since, in a previous fluores-
cence depolarization experiment, nearly identical \( r(t) \)
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Figure 4. The quantity of experimental and theoretical interest is \( G(t) \), the ensemble-averaged probability that the excitation is on the originally excited chromophore at time \( t \). The experimental \( G(t) \) results from taking the ratio of the lower to the upper anisotropy curves in Figure 3 (see eq 4). Also shown are theoretical \( G(t) \) curves calculated by using eq 8 for a 23 400 \( M_w \) PMMA chain with 20 naphthalenes. The best fit, obtained by adjusting the statistical segment length \( a \), results in an \( (R_g^2)^{1/2} \) of 37 Å. This result is in close agreement with light scattering determinations of \( (R_g^2)^{1/2} \) for a PMMA coil in a \( \theta \)-condition media. Also shown are theoretical curves at 39 (upper) and 35 Å (lower).

60 000 \( M_w \) PMMA at \( \theta \)-condition, \( (R_g^2)^{1/2} \) should be 39 ± 4 and 64 ± 7 Å, respectively. The results from the excitation transport experiments are in excellent agreement with these values.

B. Effect of the Presence of Naphthalene Groups. Although the results for the two copolymers with 0.087 mol fraction naphthalene-containing monomers agree very well with other determinations of \( (R_g^2)^{1/2} \) for \( \theta \)-condition PMMA, it is still necessary to ascertain that the presence of the chromophores does not significantly perturb the average chain conformation. This was accomplished by obtaining experimental \( G(t) \) curves for three copolymers of essentially the same molecular weight, but varying in the amount of naphthalene in the chains. These three copolymers are designated 9-23, 6-22, and 4-23 in Table II and contain 5.9, 4.0, and 4.0 mol % naphthalene-containing monomers, respectively. The samples consisted of 3/8 weight % of the desired copolymer in the 120 000 \( M_w \) host PMMA. Figure 6 shows the experimental \( G(t) \) curves obtained for these copolymers along with the theoretical best fits. The resulting values for \( (R_g^2)^{1/2} \) are 37 ± 3, 39 ± 3, and 38 ± 3 Å for the three copolymers in order from the highest to the lowest naphthalene content. These results are in qualitative agreement with solution \( (R_g^2)^{1/2} \) measurements under \( \theta \)-conditions. In addition, these results indicate that the presence of the naphthalene-containing monomers does not significantly perturb the average coil dimensions, at least up to concentrations of 9 mol % 2-VN.

Table II summarizes the results for the various copolymers in this study. A comment on the error bars associated with the measurements of \( (R_g^2)^{1/2} \) in this study is necessary. The theoretical \( G(t) \) curves at ±2 Å shown in Figures 4 and 5 are to show the sensitivity of \( G(t) \) to

Figure 5. \( G(t) \), the ensemble-averaged probability of finding the excitation on the originally excited chromophore. The experimental \( G(t) \) is for copolymer 9-60 (59 800 \( M_w \), 0.087 mol fraction 2-VN) in a 120 000 \( M_w \) PMMA host. The theoretical \( G(t) \) curves are for a 59 800 \( M_w \) PMMA chain with 49 naphthalenes. The best fit yields an \( (R_g^2)^{1/2} \) of 61 Å. The result is in very good agreement with other methods for determining \( (R_g^2)^{1/2} \) of \( \theta \)-condition PMMA. The upper and lower theoretical curves are for 63 and 59 Å, respectively.

Curves were obtained for a 20 000 \( M_w \) 2-VN/MMA copolymer in both 20 000 and 120 000 \( M_w \) PMMA hosts. Assuming that these copolymers are essentially PMMA at \( \theta \)-conditions, it is possible to compare these results with light scattering measurements of \( (R_g^2)^{1/2} \) for equivalent molecular weight PMMA in \( \theta \)-solvents. The values can be easily calculated from tabulated data. For 23 000 and

Figure 6. \( G(t) \), the ensemble-averaged probability that the excitation is still on the originally excited chromophore. Data is shown for three copolymers of essentially the same molecular weight but differing in mole fraction of 2-VN. Curve A is copolymer 4-23 (22 700 \( M_w \), 0.04 mol fraction 2-VN), curve B is copolymer 6-22 (22 400 \( M_w \), 0.059 mol fraction 2-VN), and curve C is copolymer 9-23 (23 400 \( M_w \), 0.087 mol fraction 2-VN). Also shown are the best-fit theoretical \( G(t) \) curves for equivalent molecular weight PMMA chains with the appropriate number of naphthalenes. The resulting values for \( (R_g^2)^{1/2} \) are 38, 39, and 37 Å in order from A to C. These results show that the presence of the naphthalene-containing monomers does not significantly perturb the average chain dimensions at least up to concentrations of 9 mol % 2-VN.
small changes in \((R_g^2)^{1/2}\). The reported errors in Table II are estimated from errors in the measurement of the average number of naphthalenes per chain and the weight-average molecular weight. The fact that there is really a distribution of the number of chromophores and the molecular weight does not significantly effect the result.\(^8\) The molecular weight distribution can be controlled and tested during sample preparation. The samples used in this study have sufficiently narrow molecular weight distributions to avoid problems. The effect of the distribution in the number of chromophores per chain about the average number has been tested by theoretical calculations and shown to be insignificant.\(^8\) However, error in the determination of their average values, especially in the number of chromophores per chain for the smaller copolymers can lead to errors of a few angstroms in the theoretical fit.

V. Comments and Conclusion

The accuracy of the analysis presented in this paper is determined by the validity of two key approximations: (1) the description of the energy-transfer dynamics by the first-order cumulant expansion method and (2) the use of a Gaussian chromophore pair distribution function. Although originally developed for\(^{11}\) and successfully applied to the problem of energy transfer in disordered infinite volume systems, the cumulant method can be modified to provide a highly accurate description of energy transfer in finite volume systems such as polymer coils. The modification of the method to describe transfer in infinite volume polymer systems has been described previously.\(^6\) For the number of chromophores and time scale involved in these experiments, the method is essentially exact.

Gaussian pair distribution functions are commonly employed in calculations involving freely jointed chains. Except in the limit of infinitely long polymer molecules, this description is approximate. For large chains, the use of a Gaussian distribution function is considered a very reasonable model, but for the moderate size chains studied here, the question remains open. The calculated \(G^\theta(t)\) curves are very sensitive to \((R_g^2)^{1/2}\) and, as such, provide a test of the distribution functions employed. The quantitative agreement between the \(\Theta\)-condition \((R_g^2)^{1/2}\) values determined for the 23,000 and 60,000 \(M_\text{w}\) polymer coils in solid and solution states shows that the Gaussian pair distribution function is adequate to describe these chains.

The theoretical analysis used in this paper to derive \((R_g^2)^{1/2}\) from the data is sufficiently powerful and flexible that transport observables for any pair distribution function can be calculated simply by replacing the Gaussian pair distribution function in eq 6. In fact, use of the theory in conjunction with a series of depolarization experiments covering a wide range of polymer types and molecular weights could serve to determine the applicability of the segmental distributions functions proposed for various types of polymers. However, it is necessary to be careful in drawing conclusions about model pair-correlation functions based on the qualitative shape of the theoretical \(G^\theta(t)\) curves alone. The experiment examines the pair-correlation function over a distance scale of several \(R_g\). The shape of the \(G^\theta(t)\) curves may not change significantly with the use of different mathematical models. Previous theories by Fredrickson, Andersen, and Franck\(^{14}\) and by Ediger and Fayer\(^{45}\) also predict the shape of \(G^\theta(t)\) correctly for the types of polymer blends studied here, but are in error in the quantitative determination of \((R_g^2)^{1/2}\).

\begin{table}[h]
\centering
\caption{Summary of Results}
\begin{tabular}{|c|c|c|}
\hline
\textbf{copolymer} & \textbf{\((R_g^2)^{1/2}\) determined by excitation transport} & \textbf{\((R_g^2)^{1/2}\) for equivalent \(M_\text{w}\) \(\Theta\)-condition PMMA} \\
\hline
4-23 & 38 \pm 3 & 39 \pm 4 \\
5-22 & 39 \pm 3 & 39 \pm 4 \\
9-23 & 37 \pm 3 & 39 \pm 4 \\
9-60 & 61 \pm 3 & 64 \pm 7 \\
\hline
\end{tabular}
\end{table}

\(^{6}\)From reported literature values from light scattering measurements on PMMA in various \(\Theta\)-solvents.\(^{21}\)

The finite nature of the polymer chains, which restricts the volume in which the chromophores can reside and consequently results in an inequivalence among possible chromophore positions, strongly influences the general shape of the \(G^\theta(t)\) curves. \(G^\theta(t)\) curves calculated for freely jointed chains in this paper differ significantly from both theoretical and experimental \(G^\theta(t)\) curves obtained for random isotropic chromophore distributions.\(^{76}\) However, it is expected that \(G^\theta(t)\) curves obtained, for example, for rigid rods will have a general shape quite different from those for freely jointed chains. When possible, it is useful to check the validity of the chromophore distribution model employed by making quantitative comparisons of excitation-transfer results to structural determinations by other methods such as light scattering.

These experiments demonstrate the utility of this excitation transport technique in the study of polymer blends. The technique allows quantitative determination of \((R_g^2)^{1/2}\) for isolated guest coils in a polymer matrix. The accuracy of the measurements is comparable to determinations performed with neutron scattering methods. However, we believe that the excitation-transfer technique offers greater flexibility in two ways. First, the signal-to-noise ratio achievable in excitation-transfer experiments allows measurements on blends with guest polymer concentrations that are 1 or more orders of magnitude lower than the sensitivity limits of neutron scattering. Second, and most importantly, the effect of the labeled monomer on the copolymer conformation can be ascertained by performing a series of experiments on copolymers containing various mole fractions of label. Despite the insensitivity of the present results to the mole fraction of 2-VN, label concentration dependence studies must be performed on every blend system in order to quantify the effect of label-induced perturbation. This control is not readily available to neutron scattering experiments on solid-state polymer systems.

In these experiments, we have determined \((R_g^2)^{1/2}\) for PMMA in the solid state under \(\Theta\)-conditions. The techniques and theory employed are easily extended to other solid-state systems, for example, miscible blends, phase-separated blends, or solvent-cast systems retaining substantial solvent. The effect of sample processing and history on coil conformation can also be probed. The sensitivity of excitation-transport observables to small changes in chromophore distribution coupled with the relative simplicity of time-resolved fluorescence experiments and the flexibility of the transport theory makes excitation transport induced fluorescence depolarization spectroscopy a valuable and unique tool for the study of solid-state polymer systems.

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13C NMR Study of the α-Methyl Group Rotation in Solid Poly(methyl methacrylate): Detection of the 13C T1 Minimum

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ABSTRACT: The 13C spin-lattice relaxation time of α-methyl groups in amorphous poly(methyl methacrylate) (PMMA) has been measured in the temperature range 193–388 K in two quenched samples with different tacticities. Both samples were predominantly syndiotactic, with 72.5% (s-PMMA) and 48.5% syndiotactic triads (si-PMMA). In both cases the T1C minimum was observed: centered around 160 K with nT1C = 300 ms (si-PMMA) and centered around 275 K with nT1C = 200 ms (s-PMMA). (n denotes the number of protons directly bound to the carbon in question.) Differences in T1C values as well as distinctly different shapes of the (nT1C, K/T) curves result from different sample tacticities. We propose that the high values of T1C measured at the minima result from the superposition of the α-methyl group motion and rapid fluctuations of the main chain.

Introduction

The rotation of side chains in poly(methyl methacrylate) (PMMA) has been investigated over a wide temperature range by the following techniques: dielectric1 and dynamic mechanical relaxation,2 pulsed 1H NMR,3 broad-line NMR,4 and both inelastic and quasielastic neutron scattering.5–7 Studies of the α-methyl group rotation about its Cβ axis are incomplete and often contradictory despite a large body of 13C NMR data which already exists. Such measurements have been made normally on stereoregular PMMA both in solution8–9 and in the solid state10–12 at room temperature and above; this temperature range limits the amount of useful information obtainable. The preliminary quasielastic neutron scattering investigations were similarly restricted to high temperatures because the rotation of the α-methyl group is scarcely accessible to neutrons for reasons of resolution.6 13C NMR studies conducted over a wide temperature range can provide the necessary information since they allow selective observation of a chosen resonance line in the solid state. Moreover, both the 13C spin–lattice relaxation time T1C and the chemical shift anisotropy serve as sensitive probes of molecular motion in localized environments.13–15 The quantities characterizing rotational motion, rotation rates and the activation energy, can be confidently determined from the (nT1C, K/T) plots pro-

References and Notes


2) Flory, P. J. Principles of Polymer Chemistry; Cornell University: Ithaca, NY, 1959; Chapters 10 and 12.


