Laser-Initiated Polymerization of Methyl Methacrylate: Effect of Pulse Repetition Rate and Photoinitiator Concentration on Polymerization Efficiency

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ABSTRACT: The properties and yield of the polymers produced by laser-initiated polymerization are highly dependent on the laser operating parameters. The effect of laser pulsing frequency and photoinitiator concentration on the overall yield of polymer and quantum efficiency of radical chain propagation is substantial. In general, as the interval between successive laser pulses is decreased, the overall polymerization efficiency is diminished. At higher repetition rates (greater than 3 Hz) small molecule radicals are particularly efficient in quenching or reacting with living polymer radicals. The relative number of living polymer radicals that are captured or terminated at a specific time after polymerization is initiated (by a given laser pulse) is directly related to the photoinitiator concentration.

Introduction

Since the pioneering work of Melville et al.,[1-3] the use of pulsed light sources to initiate polymerization has increased significantly. In the last few years a number of reports have surfaced dealing with the use of both pulsed and continuous output lasers as sources for initiating polymerization.[4-37] In early reports, it was clearly demonstrated that pulsed lasers, despite their propensity to create high local radical concentrations in a very short time period, were quite effective in initiating free radical polymerization. A particularly illustrative paper by Decker[7] clearly demonstrated that even an increase in the instantaneous light flux by up to 7 orders of magnitude experienced when using a pulsed nitrogen laser resulted in a relatively modest drop in the quantum efficiency for free radical propagation steps. Thus, at light intensities of 12 einstein/(s cm^2), a quantum efficiency of ~400 could be obtained with a pulsed nitrogen laser. Olaj and coworkers[14-18] recently described the use of variable laser pulsing frequency (time interval between laser pulses) to obtain kinetic rate constants for free radical polymerization.

In this paper we focus on the critical role of laser pulsing frequency and photoinitiator concentration in the molecular weight distribution of the polymers generated with a high-intensity pulsed excimer laser. By careful evaluation of polymerization conditions and laser pulse intensity, polymerization quantum efficiencies have been measured as a function of laser repetition rate and photoinitiator concentration. In addition a propagation rate constant has been calculated directly from molecular weight distribution (GPC) curves.

Experimental Section

Methyl methacrylate (MMA) (Aldrich) was passed through an inhibitor removing column, (DHR-4) supplied by Scientific Polymer Products, prior to use. The photoinitiator in this study was 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651 from Ciba-Geigy), which was recrystallized several times from methanol. The photoinitiator was added to solutions of neat MMA (9.35 M) and the optical density was adjusted to give different absorbance values. The absorbance was measured on a Perkin-Elmer spectrophotometer Model 320. Aliquots of 2 mL of the MMA photoinitiator solutions were added to a 1-cm quartz cell. Each sample was purged with nitrogen for 10 min prior to exposure to the laser. Degassing with nitrogen was continued throughout the polymerization process.

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The laser used was a Lumonics HyperEx-440 excimer laser with a xenon-fluorine fill gas mixture (output at 351 nm). The repetition rate and the number of pulses delivered was controlled with an IBM-XT PC as a triggering device. Conventional ferrioxalate actinometry was used to quantify the number of photons absorbed by the sample.[38,39] Each sample was subjected to 200 pulses, i.e., approximately 2.0×10^{18} photons. After exposure the samples were analyzed by gel permeation chromatography (GPC).

The GPC system (35 °C) consisted of a Waters 6000 psi solvent delivery pump, a Model 7010 Rheodyne injector with a 50-μL injection loop, a Waters 410 differential refractometer, and three Ultrastyragel (Waters) columns (500, 10^3, and 10^5 Å) enclosed in a Waters column heater with a tetrahydrofuran mobile phase of 1 mL/min. The GPC system was calibrated with narrow molecular weight poly(methyl methacrylate) (PMMA) and polystyrene (PS) standards from Scientific Polymer Products. The following elution volumes (V_e) were obtained for several different molecular weight standards of PMMA: MW = 840000, V_e = 17.70 mL; MW = 502200, V_e = 18.30 mL; MW = 261600, Ve = 18.90 mL; MW = 107000, V_e = 19.80 mL; MW = 98000, V_e = 19.90 mL; MW = 30000, V_e = 21.60 mL. The following elution volumes were obtained for several different molecular weight standards of PS: MW = 1860000, V_e = 16.6 mL; MW = 763200, V_e = 17.6 mL; MW = 90000, V_e = 19.9 mL; MW = 45770, V_e = 20.8 mL; MW = 17500, V_e = 22.4 mL; MW = 3550, V_e = 25.6 mL.

Results and Discussion

In recent papers,[30,32-34] we described the results obtained using a pulsed excimer laser to initiate the polymerization of methyl methacrylate (MMA). The laser was operated in two modes. In the "single-pulse" mode, laser pulses were delivered to a neat MMA sample at intervals of 10 s, thereby allowing essentially all polymer chains initiated by one pulse to terminate prior to interjection of a second pulse. The "double-pulse" mode involved introduction of two laser pulses into the MMA sample at an interval of 0.1 s. Thus, polymer chains initiated by the first pulse were prematurely terminated by small molecule radicals generated by the second pulse in the series. The double-pulse pattern was repeated every 10 s.

In the present paper, we describe results from a "multipulse" experiment where the laser is pulsed at a constant frequency corresponding to a fixed delay between each pulse. This mode of operation differs from the double-pulse mode since there is no 10-s delay period after firing the two pulses at a set interval; in other words, the multipulse mode involves continual firing of the laser at a constant repetition rate until enough of the polymer is generated (a total of 200 pulses) to allow analysis by gel permeation chromatography (GPC). Figure 1 shows GPC chromatograms of poly(methyl methacrylate) (PMMA) in

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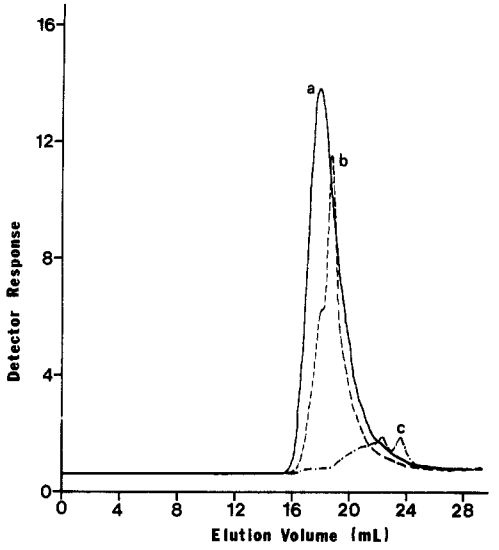

Figure 1. GPC chromatograms of poly(methyl methacrylate) at a photoinitiator optical density of 0.031 for different repetition rates: (a) 0.1 Hz; (b) 1.0 Hz; (c) 40.0 Hz.

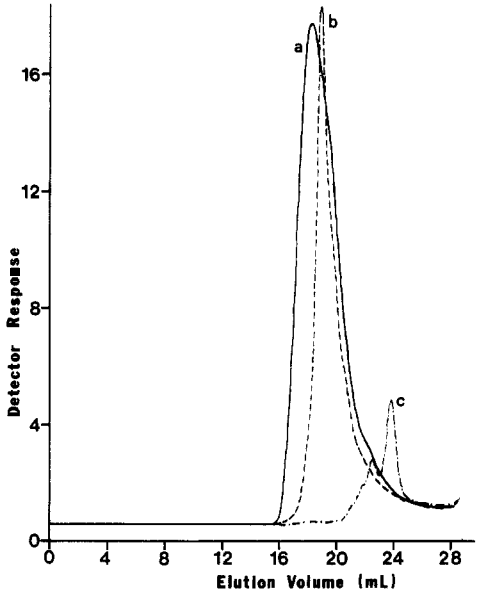

Figure 2. GPC chromatograms of poly(methyl methacrylate) at a photoinitiator optical density of 0.500 for different repetition rates: (a) 0.1 Hz; (b) 1.0 Hz; (c) 40.0 Hz.

terms of detector response (refractive index detector) versus elution volume for photoinitiated polymerization of neat MMA (photoinitiator OD = 0.031) at laser repetition rates of 0.1 Hz (10 s between pulses), 1.0 Hz (1 s between pulses), and 40 Hz (25 ms between pulses). The 0.1-Hz sample is essentially a single-pulse experiment[32] and results in a very broad molecular weight distribution. As the pulsing interval decreases from 10 s to 1 s to 25 ms two phenomena are readily apparent. First, the high molecular weight species are greatly diminished (curve b at 1-Hz operation) or totally eliminated (curve c at 40 Hz operation) when laser pulses are delivered at intervals close enough to involve premature termination of polymer radicals initiated by previous laser pulses. Second, the overall yield of polymer is severely diminished, also as a consequence of premature chain termination resulting from introduction of small molecule chain terminators while polymer radicals are still experiencing chain propagation.

Figure 2 shows results obtained for a photoinitiator concentration with an OD of 0.5. The consequences are 2-fold. There is an increase in overall polymer yield (integrated area under GPC curve) at the higher photoinitiator concentration. However, in view of the increase in light absorbed by the photoinitiator by almost an order of magnitude, the modest increase in the amount of polymer formed at a given repetition rate is quite low. This behavior can be reconciled by calculation of the polymerization quantum yield (defined as the number of chain propagation steps generated per photon of light absorbed) at the two photoinitiator optical densities. The quantum yields corresponding to OD's of 0.03 and 0.50 are 2145 and 327 at 0.1 Hz, 1112 and 195 at 1.0 Hz, and 299 and 56 at 40 Hz. The reduction in quantum yield at the higher photoinitiator concentration demonstrates the severe effect of increasing photoinitiator absorbance on polymerization efficiency. Evidently, as is expected from consideration of the basic kinetics of free radical polymerization, the introduction of large quantities (at high optical densities) of free radicals into a system in a short time results in a significantly enhanced rate of polymer chain termination. The effect of decreasing quantum efficiency with increasing photoinitiator concentration ultimately results in a decrease in overall polymer yield (relative area under GPC curve) as illustrated in Figure 3 by a log–log plot of polymer yield versus photoinitiator optical density (curve a) for laser operation at 1.0 Hz. For reference, a log–log plot of the quantum efficiency versus optical density is also shown in the same figure (curve b, Figure 3).

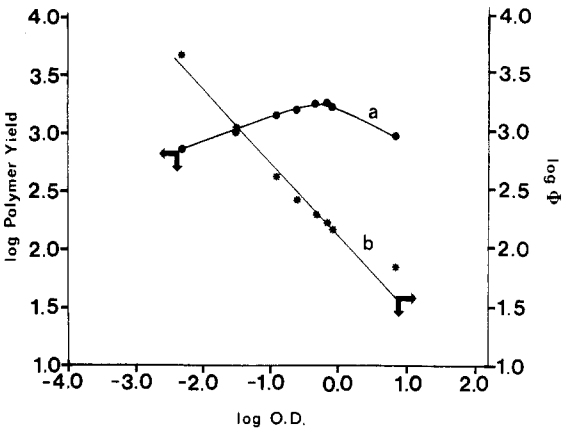

Figure 3. Plots of (a) log polymer yield versus log photoinitiator optical density and (b) log quantum yield versus log photoinitiator optical density at a constant repetition rate of 1.0 Hz (polymer yield is relative to the area under the GPC curve).

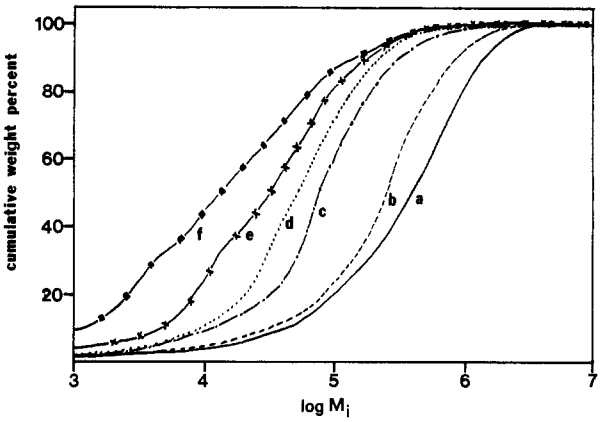

Figure 4. Plot of cumulative weight percent versus log molecular weight for poly(methyl methacrylate) at a photoinitiator optical density of 0.031 for various repetition rates: (a) 0.1 Hz; (b) 1.0 Hz; (c) 5.0 Hz; (d) 10.0 Hz; (e) 20.0 Hz; (f) 40.0 Hz.

The effect of increasing repetition rate on the polymer yield and molecular weight distribution, illustrated in Figures 1 and 2 for three laser repetition rates, can best

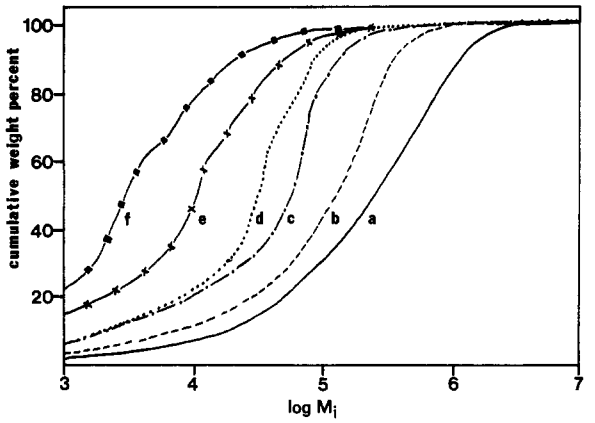

Figure 5. Plot of cumulative weight percent versus log molecular weight for poly(methyl methacrylate) at a photoinitiator optical density of 0.500 for various repetition rates: (a) 0.1 Hz; (b) 1.0 Hz; (c) 5.0 Hz; (d) 10.0 Hz; (e) 20.0 Hz; (f) 40.0 Hz.

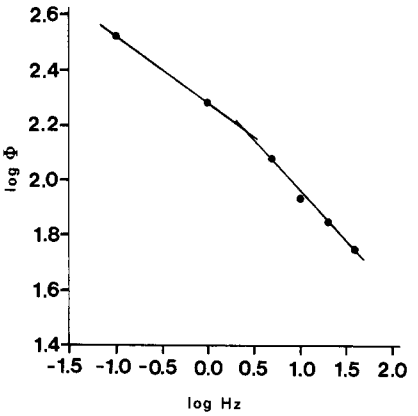

Figure 6. log–log plot of quantum yield versus repetition rate for poly(methyl methacrylate) at a photoinitiator optical density of 0.500.

be described by cumulative weight precent versus log molecular weight plots for a whole series of pulsing frequencies ranging from 0.1 to 40 Hz (Figures 4 and 5). Both Figure 4 and 5 clearly demonstrate the decrease in high molecular weight polymer as a function of repetition rate. For example, for the sample with photoinitiator OD = 0.031 at a repetition rate of 0.1 Hz, over half (by weight) of the polymer has a molecular weight greater than ~ 400 000. In contrast, at a repetition rate of 40.0 Hz, half of the polymer (by weight) has a molecular weight of less than ~13 000 and there are virtually no polymers with molecular weight much above 400 000. Similar conclusions can be reached from the data in Figure 5. As in the case of increasing photoinitiator optical density at a constant laser repetition rate, an increase in the laser pulsing frequency also results in a decrease in the quantum yield (ϕ) for polymerization (Figure 6). The log–log plot of ϕ versus laser repetition rate in Figure 6 illustrates yet another important phenomenon concerning laser-initiated polymerization. There is a change in the slope in Figure 6 that occurs at a repetition rate corresponding to a frequency of approximately 3 Hz. Thus, at repetition rates greater than about 3 Hz, the small molecule radicals produced by a given laser pulse are somewhat more effective in terminating polymer radicals generated by previous pulses. (Incidentally, the efficiency at which a given laser pulse will produce small molecule radical terminators will depend in a complicated fashion on the optical density of the photoinitiator.) Increased termination efficiency at higher repetition rates might well be related to an enhanced susceptibility for radical termination for polymer radicals

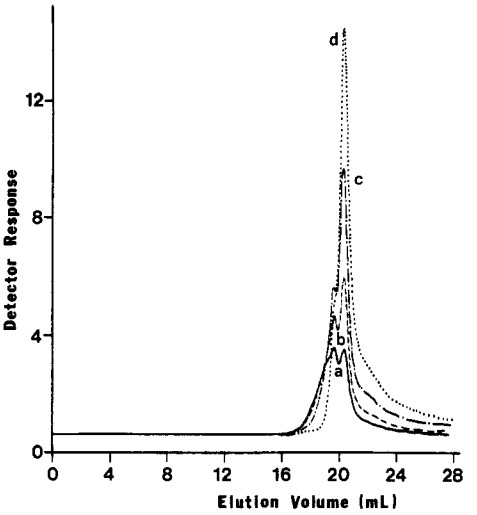

Figure 7. GPC chromatograms of poly(methyl methacrylate) generated by firing the laser at a constant repetition rate of 5 Hz for several different photoinitiator optical densities: (a) OD = 0.005; (b) OD = 0.031; (c) OD = 0.124; (d) OD = 0.823.

with a kinetic chain length less than about 1000 monomer units (see ref 40). This corresponds to the range over which polymer termination rate constants are known to decrease with increasing chain length.

Another fundamental aspect of laser-initiated polymerization can be illustrated by selecting a particular pulsing frequency (5 Hz) and recording the GPC chromatograms for a series of photoinitiator concentrations, paying particular attention to the relative peak heights of the individual modes in the curves. Although chromatograms were recorded for a large number of samples with widely varying photoinitiator concentration, results are only shown in Figure 7 for four concentrations spanning 2 orders of magnitude. The chromatogram (curve a) obtained with the lowest photoinitiator concentration shows two sharp, distinct peaks with broad shoulders on the high molecular weight side (low elution volume). The two narrow peaks have maxima occurring at molecular weight values [determined by calibration with both poly(methyl methacrylate) and polystyrene standards] of 132 000 and 60 000. The peak at the lowest molecular weight corresponds to termination of living polymer radicals generated from the previous or first pulse and still propagating at the time of firing of the second pulse (200 ms later). The higher molecular peak results from reaction of small molecule radicals generated by the "third" pulse (400 ms after the first pulse) with living polymer radicals that were initiated by the first laser pulse fired two pulses previously and that survived termination by small molecule quencher radicals produced by the second pulse. The absence of a distinct third peak at the higher concentrations indicates the efficiency of the coupling of the small radical and the growing polymer radical; i.e., most of the polymer radicals produced by a given laser pulse are effectively terminated by small molecule radical species from the next two pulses. Of course the radicals produced by the so-called second and third pulses may also initiate new polymer radicals. Curves b–d in Figure 7 show that as the photoinitiator concentration increases, the relative ratio of the low molecular weight peak (at 20.4-mL elution volume) to the higher molecular weight peak (at 19.6-mL elution volume) increases. This reflects an enhancement of primary chain terminator radical concentration such that an increasing number of polymer radicals produced by a given pulse are terminated upon firing the next pulse into the sample. In fact, at a photoinitiator OD of 0.82 the lower molecular

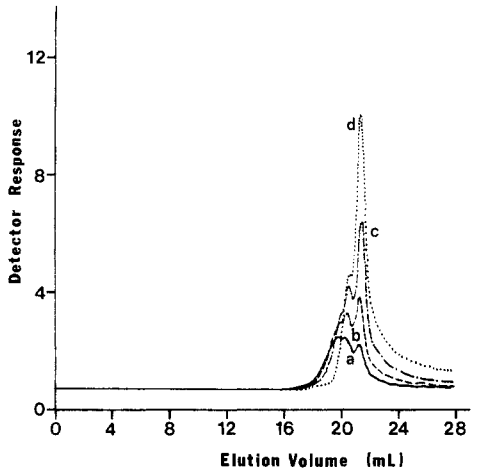

Figure 8. GPC chromatograms of poly(methyl methacrylate) generated by firing the laser at a constant repetition rate of 10 Hz for several different photoinitiator optical densities: (a) OD = 0.005; (b) OD = 0.031; (c) OD = 0.124; (d) OD = 0.823.

weight peak appears almost exclusively and the high molecular weight peak only gives a small shoulder. Before concluding discussion of the results in Figure 7, it is worth noting the propagation rate constants for the polymerization can be obtained by knowing the delay time between firing of laser pulses and the molecular weight of the peak maxima in the GPC curves. For example in Figure 7 (curve c), a value of 320 L mol^{-1} s^{-1} is calculated for the rate constant of polymerization of MMA by using the low molecular weight peak (20.4 mL; MW = 60 000) and a value of 353 L mol^{-1} s^{-1} is calculated from the higher molecular weight peak (19.6 mL; MW = 132 000). These two values are in fairly good agreement with data reported previously.[41]

Similar results to those in Figure 7 have been obtained for operation at 10 Hz (Figure 8). As seen in Figure 8, there are three distinct peaks in the 10-Hz samples at the lower photoinitiator concentrations (curves a and b, Figure 8), whereas there are two peaks in the 5-Hz samples in Figure 7. Apparently, the peaks in Figure 8 represent premature termination of the living polymer (produced by a given pulse) at intervals of 100, 200, and 300 ms. The 200 ms or second peaks in Figure 8 (curves a–d) all occur at the same position (molecular weight or elution volume) as the 200 ms or first peaks in Figure 7. At the lower concentrations (curves a and b, Figure 8) all of the living polymer radicals generated by any one laser pulse are effectively terminated by interjection of small molecule terminator radicals generated from the next three pulses. As the photoinitiator concentration is increased, the polymer chains are more effectively terminated with each, subsequent pulse (referenced to a specific pulse arbitrarily designated as the chain-initiating pulse), until at the highest concentration (curve d, OD = 0.82) employed in this study most of the chains are terminated by two pulses subsequent to the chain-initiating pulse. This is essentially the same results obtained for the 5-Hz samples in Figure 7.

In order to provide a basic kinetic analysis for peaks in the molecular weight distributions in Figures 1, 2, 7, and 8, the kinetic eq 1 has been developed (ref 32–34)

$$A_i = \frac{1}{2}\left(\frac{[R^\bullet]_0}{1 + k_t[R^\bullet]_0 t}\right)\left(\frac{\gamma^i e^{-\gamma}}{i!}\right) \qquad (1)$$

where A_i = distribution of "living" (growing) polymer chains, k_t = kinetic rate constant for termination, $[R^\bullet]_0$ = total radical concentration in polymerizing medium at time $t = 0$ following initiation by the laser pulse, $\gamma = k_p[M]t$ = average kinetic chain length of the living polymer chains, i = the degree of polymerization, and t = elapsed time between laser pulses. This equation describes the living polymer molecular weight distribution at a given time after firing the so-called first laser pulse.

Equation 1, which results from solving the kinetic equations describing a non-steady-state free radical polymerization process, is similar to the Poisson distribution for an anionic polymerization process and describes the concentration of living polymer chain with degree of polymerization "i", where all of the chains are initiated at the same instance by a laser pulse. The second term in eq 1 is strictly a Poisson distribution, while the first term takes into account the total radical depletion as a result of chain termination. The result of eq 1 is a slightly broadened Poisson distribution describing the living polymer chain distribution. The sharp peaks in Figures 1, 2, 7, and 8 correspond to polymer fractions generated by quenching the living polymer distribution at particular instances in time following the initial laser pulse. A computer simulation of multiple-pulse GPC data similar to that presented in this paper has been described in several recent publications and will not be reproduced here.[30,32–34]

Conclusions

This paper illustrates the dramatic effect of the laser repetition rate and the photoinitiator concentration on the polymerization efficiency of methyl methacrylate. It has been clearly demonstrated that an increase in the laser repetition rate results in a decrease in both the amount and molecular weight of the polymer generated. Due to a decrease in the polymerization quantum efficiency, there is a distinct maximum obtained in the polymer yield with increasing photoinitiator concentration. From a critical evaluation of the dependence of the polymerization quantum yield on the laser repetition rate, it was postulated that large polymer radicals are less susceptible to premature chain termination from small molecule radicals than their lower molecular weight (DP < 1000) counterparts. Finally, a rate constant for polymerization was calculated from a knowledge of the pulse repetition rate and maxima in the molecular weight distribution curves for the polymers generated. It should be noted that a kinetic study of laser-initiated polymerization has just recently been published by O'Driscoll et al.[42] in which rate constants were also obtained.

Our results clearly indicate the potential of using controlled pulsed laser sources to evaluate polymerization kinetics of simple monofunctional monomers. Future work in this area will center on laser-initiated polymerization of multifunctional monomers.

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Registry No. PMMA, 24650-42-8; 2,2-dimethoxy-2-phenylacetophenone, 9011-14-7.

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Uniting Molecular Network Theory and Reptation Theory To Predict the Rheological Behavior of Entangled Linear Polymers

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ABSTRACT: A new model is presented for the description of the linear viscoelastic behavior of entangled linear polymer chains. The equations are derived by combining the structure of molecular network theory, the concept of forced segmental reptation around entanglement junctions, and the reptation description of path length. The resulting equations for monodisperse melts show crossover with the Rouse equation at $M/M_e = 3.21$ and crossover with a modified tube diffusion result at $M/M_e = 380$. Over two decades of molecular weight, a result close to $\eta_0 \sim M^{3.4}$ is obtained. The equations also predict a value of $J_e^0G^0$ of 2.462 for monodisperse melts. An explicit equation for the viscosity of binary blends is obtained, which agrees well with the empirical rule $\eta_0 \sim M_w^{3.5}$. Further comparisons to the steady shear compliance J_{e_b} and loss modulus data for binary blends of polybutadiene demonstrate good predictive ability of the complete relaxation spectrum. As this theory describes molecular motions that are imposed by the deformation, it is consistent with self-diffusion data showing $D \sim M^{-2}$. The quantitative agreement of the two constants with accepted values lends considerable support that the modes of motion described are a realistic description of the molecular dynamics.

Introduction

The effect of molecular weight and molecular weight distribution on the chain dynamics of entangled linear polymer chains has been a subject of intense interest for 30 years. Since the early Graessley theories,[1,2] many approaches have been tried to describe the observed behavior. It has been well established experimentally that the zero-shear viscosity η_0 can be well correlated with the weight-average molecular weight $\bar{M}_w$ by the expression

$$\eta_0 = K\bar{M}_w^{\alpha} \quad (1)$$

where α varies only slightly from polymer to polymer from 3.3 to 3.6.[3,4] This is generally true for all molecular weights above a critical molecular weight, M_c, where M_c is approximately $2M_e$ and M_e is the molecular weight between entanglements as defined by the shear modulus G^0

$$G^0 = \rho RT/M_e \quad (2)$$

where ρ is the polymer concentration, R is the universal gas constant, and T is the temperature. Both the shear modulus G^0 and the steady-state compliance J_e^0 are independent of molecular weight for monodisperse systems above M_c and the product $J_e^0G^0$, which is a measure of the breadth of the spectrum of chain motions, is generally

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