Vapor Phase Osmometry. The number-average molecular weights of the species formed upon polymerization of vesicles prepared from **4** and from mixtures of 40% **4** and 60% **2** were determined to be 3010 and 1500, respectively, by vapor phase osmometry. The corresponding degrees of polymerization, 5.1 and 2.5, indicate the formation, on the average, of small oligomers and dimers. These low degrees of polymerizations are in accord with those assessed from the laser-initiated photopolymerizations (Table IV).

Conclusion

Unequal distribution of neutralized ion pairs and charged species in photopolymerized vesicles prepared from mixtures of negatively (**4**) and positively (**2**) charged surfactants is the most significant result of the present study. The observed two-phase transitions were attributed to **4** + **2** ion pairs and to separated patches of **4** in the vesicle matrices. The importance of domains is that they provide a mechanism for releasing the contents of vesicles.[3] Kinetic measurements of photopolymerization, as well as vapor phase osmometry, indicated very small degrees (2-5) of photopolymerizations. With the exception of one report,[19] similar small degrees of polymerizations[15,20,21] were observed for vesicles prepared from styrene-containing surfactants.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. 4, 116437-66-2; 4 (homopolymer), 116437-67-3; 4/2, 116466-63-8; 4/2 (homopolymer), 116466-65-0; 5, 116437-64-0; 6, 116437-65-1; $POCl_3$, 10025-87-3; 4-vinylbenzoyl chloride, 1565-41-9; hexadecyl alcohol, 36653-82-4; $H_2N(CH_2)_{10}CO_2CH_3$, 28691-27-2.

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Laser-Initiated Polymerization of Methyl Methacrylate: Repetition Rate Effect on Molecular Weight Distribution

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ABSTRACT: The critical effect of the pulsing frequency on the molecular weight distribution of the laser-initiated polymerization of methyl methacrylate has been characterized. High laser repetition rates (i.e. 40 Hz) result in a significant decrease in polymer yield as well as a marked change in the structure of the molecular weight distribution curves. The individual peaks observed in the GPC of the poly(methyl methacrylate) generated are simulated by a series of successive Poisson distribution functions.

In the past few years there have been a number of reports dealing with the use of pulsed lasers as sources to free radical polymerization.[1-20] Due to the immense industrial and technical interest in lasers as candidates for imaging and photoresist processing,[4] basic studies that describe the kinetics and mechanisms of laser-initiated

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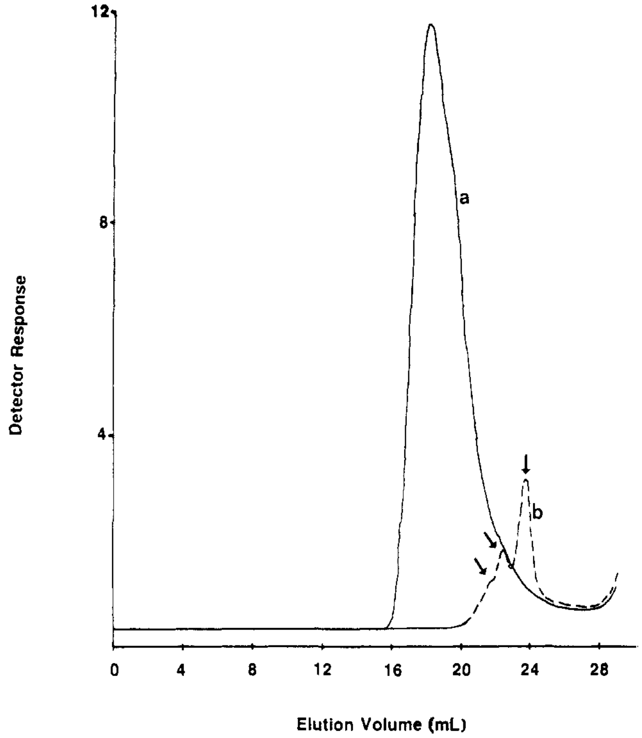

Figure 1. GPC chromatograms of poly(methyl methacrylate) generated by firing laser with repetition rate: (a) 0.1 Hz, —; (b) 40 Hz, --- (photoinitiator OD = 0.495 at 351 nm).

polymerization are critical in assuring continued advancement in laser processing of photopolymer systems. In a key paper on laser polymerization of multifunctional acrylated monomers, Decker[1] demonstrated that a pulsed nitrogen laser source was quite effective in generating highly cross-linked networks at relatively high (6–20 pulses/s) laser repetition rates. Likewise, we have clearly shown that both pulsed nitrogen and excimer lasers can effectively be used to study the free radical kinetics of multifunctional monomers.[18-20] Despite the initial reports on laser-initiated polymerization of radical chain processes, a critical and most important feature of laser-initiated polymerization that has received relatively little attention deals with the effect of high laser repetition rates (>10 pulses/s) and short delay times (<0.1 s) between pulses on the polymerization kinetics and the molecular weight distribution of the polymers produced. It is this aspect of laser-initiated polymerization that is explored in this paper on molecular weight distributions of polymers generated by a high-intensity pulsed xenon fluoride excimer laser (λ_{ex} = 351 nm). A simple kinetic model is employed to simulate the GPC curves of poly(methyl methacrylate) (PMMA).

Two polymer samples of PMMA were produced by firing the laser into a neat methyl methacrylate sample with a concentration of 2.27×10^{-3} M 2,2-dimethoxy-2-phenylacetophenone photoinitiator (OD = 0.495 at 351 nm) (OD = optical density) at repetition rates of 0.1 and 40 Hz corresponding to delay times between successive pulses of 10 s and 25 ms, respectively. The samples will be designated accordingly as the 0.1- and 40-Hz samples. In each case 200 pulses were absorbed by the nitrogen degassed samples contained in a 1 cm × 1 cm × 3 cm quartz cell. Since the number of photons impinging on the sample through an orifice with 0.211-cm diameter was constant at 1.1×10^{16} photons per pulse as determined by ferrioxalate actinometry, the total number of photons absorbed by each sample was constant at 1.47×10^{18}. Figure 1 shows GPC chromatograms (tetrahydrofuran mobile phase; 500-, 10^3-, and 10^5-Å Ultrastyragel columns) of the two polymer samples. Two observations can be readily made. First, polymerization initiated by the laser at a repetition rate of 40 Hz is much less efficient in terms of percent conversion (proportional to the total area under the GPC chromatogram) than for 0.1 Hz even though each sample absorbs the same total number of photons. Second, the GPC chromatogram of the 40-Hz polymer sample is characterized by a general shift to lower molecular weight (longer elution times) species and the appearance of three distinct peaks with retention times of 21.76, 22.40, and 23.76 min. (For comparison, poly(methyl methacrylate) standards with molecular weights of 107 000 and 30 000 have retention times of 19.8 and 21.6 min, respectively, on the same GPC apparatus). In order to better visualize the effect of laser repetition rate on the molecular weight distribution of the polymers produced, Figure 2 shows cumulative weight percent versus log (molecular weight) plots for the 0.1- and 40-Hz samples. Perhaps even more vividly than the raw GPC chromatograms, the cumulative weight percent curves in Figure 2 illustrate the dramatic effect of laser repetition rate on the molecular weight of the polymers generated. For example, from Figure 2 one can deduce that the 40-Hz sample has 60 wt % of the polymers with a molecular weight of 5000 or less and virtually no species with molecular weight above 100 000. Conversely, the 0.1-Hz sample has over 90 wt % of the polymers with molecular weight greater than 25 000 and 50 wt % greater than 300 000. In fact 20 wt % of the 0.1-Hz sample has polymers with molecular weight over 1 000 000. Obviously an astounding difference in the molecular weight distribution of two polymer samples produced by laser-initiated polymerization can be created by simply varying the time delay pattern between laser pulsing.

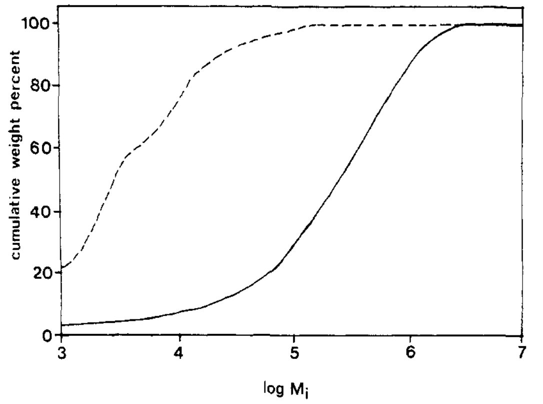

Figure 2. Plot of cumulative weight percent versus log molecular weight generated by firing laser with repetition rate: (a) 0.1 Hz, —; (b) 40 Hz, ---.

Having established the pronounced effect of laser repetition rate on both the yield of polymer and its molecular weight distribution, we now turn to a brief description of a mathematical kinetic model of laser-initiated polymerization which takes into account the effect of repetitive pulses on the molecular weight distribution of the polymers generated. Scheme I shows a simple mechanistic model of photoinitiated polymerization. Upon absorption of a single photon of light by the photoinitiator I, two radical species ($X^\bullet$ and $Y^\bullet$) are formed. For purposes of our kinetic development it is assumed that only one of the radicals formed ($X^\bullet$) adds to a monomer unit M and initiates the chain growth process. If the pulse interval is long enough to allow virtually all the free radicals to couple prior to the next pulse, then each pulse will generate the same molecular weight distribution, provided that the monomer

Scheme I

initiation

$$\mathrm{I} \xrightarrow{h\nu} \mathrm{X}^{\bullet} + \mathrm{Y}^{\bullet}$$

propagation

$$\mathrm{X}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{XM_1}^{\bullet}$$

$$\mathrm{XM_1}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{XM_2}^{\bullet}$$

$$\vdots$$

$$\mathrm{XM}_{i-1}^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{XM}_i^{\bullet}$$

termination

$$\mathrm{XM}_i^{\bullet} + \mathrm{Y}^{\bullet} \xrightarrow{k_T} \mathrm{XM}_i\mathrm{Y}$$

$$\mathrm{XM}_{i-j}^{\bullet} + \mathrm{XM}_j^{\bullet} \xrightarrow{k_T} \mathrm{XM}_i\mathrm{X}$$

$$i > 0 \text{ and } 0 \leq j < i$$

concentration and optical density do not change appreciably over the course of the polymerization.

The growing polymer chains at any given instant can either undergo addition to another monomer unit, or they can couple with another free radical species. The probability (P) of undergoing propagation is

$$P = \frac{k_p[\mathrm{M}]}{k_p[\mathrm{M}] + k_t(2[\mathrm{W}^{\bullet}] + [\mathrm{C}^{\bullet}])} \qquad (1)$$

where k_p and k_T are the rate constants for propagation and termination, respectively. [W•] is then the total concentration of small molecule free radicals (X• + Y•) while [C•] is the concentration of all growing polymer radical chains. The probability of coupling two growing chains or coupling a growing chain with a nonpropagating free radical species (Y•) is similarly defined. The former termination results in a polymer molecule twice the size of the latter. For sufficiently long pulse intervals, the free radical concentration gradually decreases to a negligible value, thus leading to a limiting molecular weight distribution. This limiting distribution has two components. Part of the distribution may arise from polymer chains terminated by the nonpropagating free radical species [Y•]. Distributions such as these have been extensively studied.[21] However, that part of the distribution generated by the coupling of growing chains is more complex and will be treated in a subsequent paper that employs generating functions to solve a series of product distribution functions.

As the pulse interval is decreased, some growing chains will still exist when the next pulse occurs. This second pulse will cause a sudden increase in free radical species resulting in the premature termination of a large fraction of the chains generated by the former pulse. Therefore, a peak corresponding to the number of monomers added between pulses will be expected in the molecular weight distribution. By extending this argument further and considering that a fraction of chains generated by a given pulse will survive multiple subsequent pulses, one must then conclude that there will exist a specific peak in the molecular weight distribution for each subsequent pulse. Though the assumption of abruptly terminated living polymer chains is not a complete description of the process under consideration, it does illustrate the origin of multiple peaks in the molecular weight distribution obtained at high repetition rates (40 Hz). Figure 3 shows an expanded plot of relative mass versus elution volume. Figure 4 shows a similar plot of relative mass versus elution volume that is generated by superimposing a series of computer generated Poisson distributions. The computer simulation treats the case of a living polymer which undergoes partial termination at regular intervals. The first Poisson peak in the computer simulation in Figure 4 was chosen to correspond to the elution volume experimentally measured for the low molecular weight peak (longest retention time) in Figure 3. By comparison of Figures 3 and 4, one can conclude that experimentally determined molecular weight distributions for polymers produced by using the 25-ms (40-Hz) pulse intervals are comparable in structural features to the multiple Poisson distributions. This suggests that the multiple peaks observed in the GPC data for the 40-Hz samples are consistent with the simple kinetic model described herein. The computer simulation gives rise to the narrowest peaks possible for a synthetic polymer. The experimental peaks are somewhat broader due to a noninstantaneous termination of the growing chains. The implications of this analysis are quite far reaching in terms of providing a method of probing the reaction kinetics of free radical chain processes. The variance in the distribution breadth and peak maxima will be treated rigorously in a full paper. In addition, the effect of photoinitiator concentration on the polymer yield and molecular weight

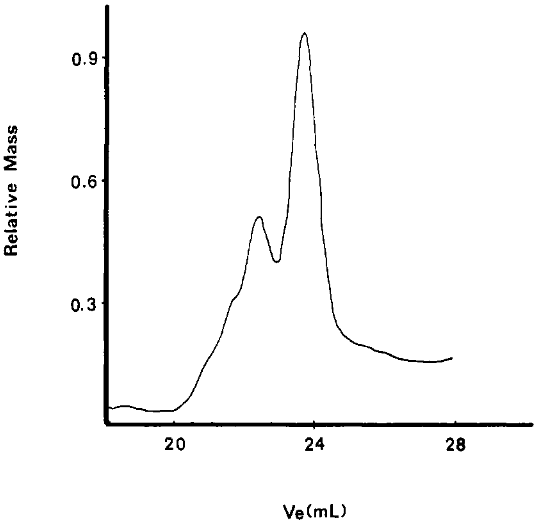

Figure 3. Plot of relative mass versus elution volume (V_e) for poly(methyl methacrylate) generated by firing laser with repetition rate of 40 Hz (photoinitiator OD = 0.495).

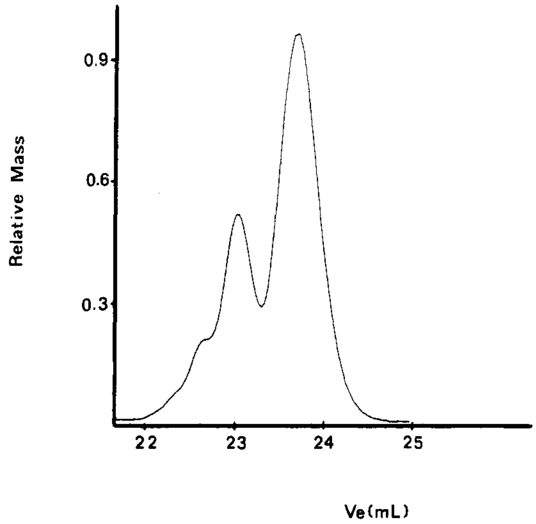

Figure 4. Plot of relative mass versus elution volume (V_e) for poly(methyl methacrylate) simulated by computer based on a series of Poisson distributions.

distribution will be considered.

In conclusion, we have demonstrated the pronounced effect of laser repetition rate on the molecular weight distribution of photopolymerized methyl methacrylate. The narrow peaks found in the GPC chromatogram of poly(methyl methacrylate) generated by firing the laser at a repetition rate of 40 Hz (25 ms between successive pulses) have been initially described by a simple kinetic model based upon a series of Poisson distribution functions. Complete details of the computer simulation of the molecular weight distributions as a function of pulsing frequency as well as several refinements to our current approach, will be published in a full paper. This paper serves to provide a basis for describing the crucial effect of laser parameters on the polymerization of monofunctional monomers. Extension of this work to encompass multifunctional monomers is in progress.

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Registry No. PMMA, 9011-14-7.

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Preparation and Polymerization Behavior of 2,4-Dicyanostyrene and 2,4,6-Tricyanostyrene

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ABSTRACT: 2,4-Dicyanostyrene (DCS) was successfully prepared in 18% yield via a series of six reactions and 2,4,6-tricyanostyrene (TCS) was barely in 0.15% yield via five reaction steps. It was found that DCS and TCS are polymerizable with radical and anionic initiators. DCS and TCS are copolymerizable in a random and an alternating fashion, respectively, with styrene (St) in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) in acetonitrile to afford the monomer reactivity ratios r_1(DCS) = 1.85 ± 0.03 and r_2(St) = 0.08 ± 0.03 for the DCS–St system at 60 °C and r_1(TCS) = 0.02 ± 0.02 and r_2(St) = 0.04 ± 0.01 for the TCS–St system at 60 °C. By using these values, the Alfrey–Price's Q and e values were determined to be $Q = 4.10$ and $e = +0.58$ for DCS and $Q = 2.83$ and $e = +1.86$ for TCS. When DCS or TCS was mixed with p-(dimethylamino)styrene (DMASt), the former system was colored pale yellow and did not undergo further reaction, while the latter one was colored red and underwent spontaneous reaction to give polymeric product containing homopolymers of TCS and DMASt, suggesting that anionic polymerization of TCS and cationic one of DMASt occur at the same time.

Introduction

Only a few compounds have been reported of the electron-accepting group substituted styrenes carrying more than two strongly electron-withdrawing groups on the benzene nucleus, such as 2,4,6-trinitrostyrene (TNS),[1-3] 2,4,6-tris(trifluoromethyl)styrene (TFS),[4] and 2,5-, 3,5-, and 3,4-bis(trifluoromethyl)styrenes.[5] Although the cyano ($\sigma_p = 0.674$)[6] group is strongly electron withdrawing and its character is just intermediate between that of nitro ($\sigma_p = 0.778$)[6] and trifluoromethyl ($\sigma_p = 0.532$)[6] groups, polycyano-substituted styrenes have not yet been found in any literature, but *o*-, *m*-, and *p*-monocyanostyrenes[7-9] were reported. In addition, because the cyano group appears to be almost insensitive to free radical species compared with the nitro group, it was expected that polycyano-substituted styrenes would be readily polymerizable with a free radical initiator while TNS is not so polymerizable.[1,2]

In this work, 2,4-dicyanostyrene (DCS) and 2,4,6-tricyanostyrene (TCS) were first prepared as new polycyanosubstituted styrenes, and their polymerization behaviors were studied.

Experimental Section

***p*-Bromoethylbenzene (1).**[10] *p*-Bromoacetophenone (83.7 g, 0.42 mol) was reduced with zinc amalgam[11] which was prepared

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