Communications to the Editor

Narrow Polydispersed Reactive Polymers by a Photoinitiated Free Radical Polymerization Approach. Controlled Polymerization of Methyl Methacrylate

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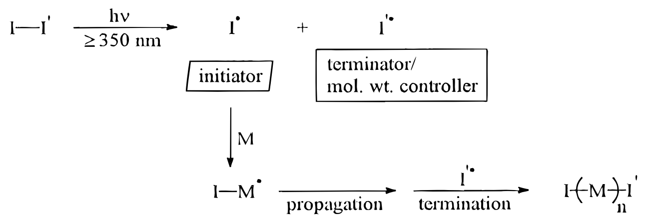
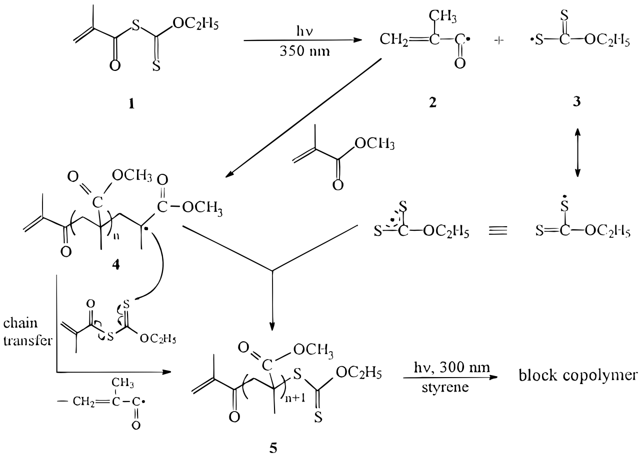
Accurate control of polymerization processes leading to well-defined end functional macromolecular architectures with narrow polydispersity has great significance in polymer research. Traditional "living" polymerization methods such as stepwise, group-transfer, ionic, or coordination processes suffer from rigorous synthetic requirements and incompatibility with a variety of monomers.[1−6] In this context, synthesis of narrow polydispersed polymers with controlled molecular weights and well-defined end functional groups using free-radical chemistry has attracted the attention of polymer chemists in recent years. Even though conventional free-radical polymerization strategies are synthetically less rigorous, they lack the ability to accurately control molecular weights and end functional groups, leading to polymers with broad molecular weight distributions. This is mainly due to the uncontrollable termination processes of the growing polymer radicals. Thus, the concept of "living" free radical polymerization has been introduced by which accurate control of the molecular weight and polydispersity can be achieved.[7] However, majority of the studies in this direction are restricted to thermal "living" free radical mechanisms.[8−10] The photo "iniferter" concept introduced by Otsu et al. is an exception in which photolytically generated sulfur-centered radicals react reversibly with the growing polymer chain ends.[11] However, the polymers obtained by the "iniferter" approach were found to have high polydispersities similar to conventional free radical processes.

In the present communication, we describe a novel photoinitiated free radical approach for the synthesis of narrow polydispersed poly(methyl methacrylate) (PMMA) with predetermined molecular weights and reactive end functional groups under mild photolytic conditions. The success of the present approach is the use of a novel photoinitiator which decomposes to give two unsymmetrical free radicals with distinctly different reactivities toward a polymerizable monomer (Scheme 1). In this case, one of the radicals acts as initiator while the other radical is a stable species with a high primary radical termination efficiency, thereby considerably decreasing the chances of termination by polymer radical recombination and disproportionation reactions. Thus, significant control over the termination process could be achieved, leading to the formation of narrow polydispersed polymers.

Scheme 1



Scheme 2



S-Methacryloyl *O*-ethyl xanthate (MAX) has been chosen as the photoinitiator mainly because of its easy synthetic accessibility and inability to undergo self-polymerization.[12] Moreover the use of MAX as photoinitiator would provide polymers with reactive end functional groups. On the basis of the earlier reports on the photodissociation of acyl and aroyl xanthates,[13] it is reasonable to anticipate that MAX undergoes homolytic bond cleavage, leading to the methacryloyl radical **2** and the resonance-stabilized thiocarbonylthiyl radical **3** as shown in Scheme 2. In the presence of an excess of the monomer, **2** would initiate the polymerization, whereas **3** would acts as the molecular weight controller by primary radical termination even though, in principle it can also initiate polymerization. However, the inert nature of thiocarbonyl thiyl radicals toward vinyl monomers and their high affinity for termination reaction is well-documented in the literature.[14] This mechanism will leads to polymers with a photoactive (300 nm or below) thiocarbonylthiyl group at the tail end of the polymer. This can be supported by the earlier observation of Zard and co-workers of the photochemical addition of *S*-acyl xanthates to unsaturated compounds.[15]

Irradiation of MMA in the presence of MAX at 32 °C under 350 nm light showed a linear conversion of the monomer with time, particularly under low monomer

Table 1. Effect of MAX Concentration on R_p, M_n, and Polydispersity for the Photopolymerization of MMA[a]

run	[I] × 10^3, M	% conversion	$R_p \times 10^4$, M s^{-1}	$M_n \times 10^{-4}$	polydispersity (*D*)
1	2.5	10	2.9	2.7	1.3
2	5	15	4.4	2.5	1.3
3	7.5	16	4.6	2.2	1.3
4	10	19	5.2	2.0	1.3
5	25	17	4.9	1.8	1.4
6	50	15	4.1	1.7	1.4

[a] [MMA] = 5 M, time = 30 min, I = MAX, λ_{irr} = 350 nm, and temp = 32 °C.

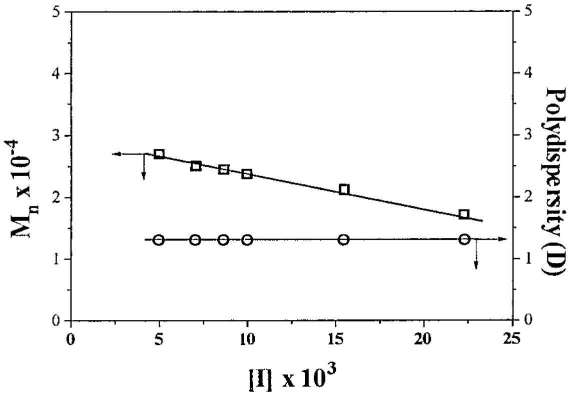


Figure 1. Effect of MAX concentration on M_n and polydispersity (*D*) of MMA polymers. [MMA] = 5 M.

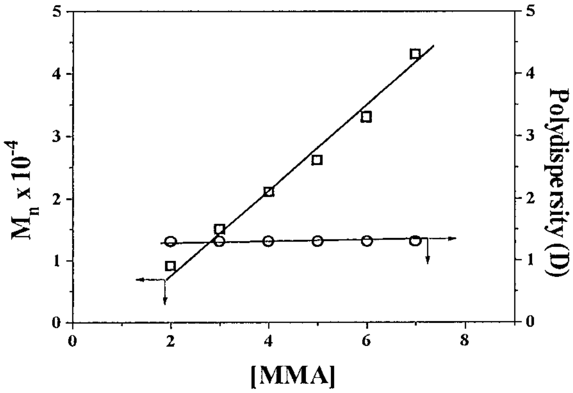


Figure 2. Effect of MMA concentration on M_n and polydispersity (*D*) for the photopolymerization using MAX (5 × 10^{-3} M).

conversions. The rate of polymerization (R_p) under such conditions showed a linear relationship with the square root of the initiator concentrations. However, under higher initiator concentrations (>2 × 10^{-2} M) considerable deviation from the linearity could be noticed. This could probably be due to a chain transfer reaction by the undissociated MAX. Results of the preliminary studies on the photopolymerization of MMA using various concentrations of MAX are shown in Table 1. Molecular weights of polymers obtained are found to decrease with increase in MAX concentrations, whereas the polydispersity indices (*D*) remain unaffected (Figure 1). On the other hand, a linear increase in the molecular weights is observed with increase in MMA concentrations (Figure 2). Interestingly, the polydispersity indices in all the cases were practically unaffected by the initiator or monomer concentrations and remained lower (M_w/M_n <1.5) than the theoretical value for a conventional free radical polymerization.

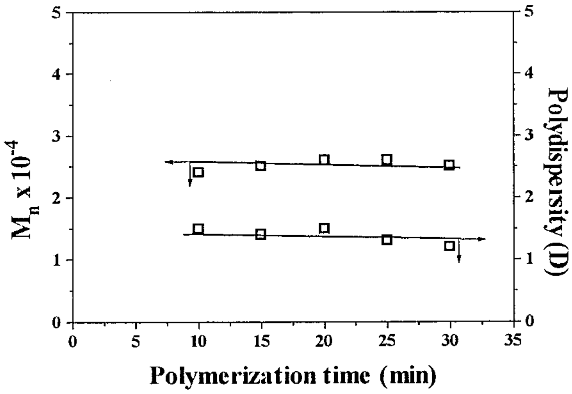


Figure 3. Effect of irradiation time on M_n and polydispersity for the photopolymerization of MMA (5 M). [MAX] = 5 × 10^{-3} M.

Effect of irradiation time on molecular weights and polydispersities are shown in Figure 3. In contrast to the "living" free radical polymerization, molecular weights of polymers remain constant, independent of the monomer conversion. The end group analysis of polymers by elemental sulfur analysis has revealed an average of one thiocarbonyl thiyl group for every polymer chain. This observation indicates that most of the thiocarbonylthiyl radicals are mainly involved in the termination process. The presence of the end functional groups in polymer **5** is clear from the IR absorptions around 1729 (C=O), 1606 (C=C), 1255, and 1043 cm^{-1} (C=S). ^1H NMR spectral analysis revealed the presence of weak resonance peaks at δ 4.5 and 1.45 due to the *O*-ethyl moiety of the thiocarbonylthiyl group. However, the presence of the methacryloyl group in polymer **5** was not very clear from the ^1H NMR spectrum. The end thiocarbonylthiyl group of polymer **5** is not photodissociable under 350 nm irradiation, which prevents any reversible addition of monomer. On the contrary, irradiation of **5** in the presence of monomers such as styrene under 300 nm light at 32 °C provided block copolymers of **5** with enhanced molecular weight, indicating the presence of an end-capped thiocarbonylthiyl group. In this case the molecular weight of the block copolymer was found to increase with time of irradiation as in the case of a "living" free radical polymerization.

The above results reveal that, even though the photopolymerization of MMA using MAX has the characteristic of a simple free radical polymerization, its termination step is basically different from the conventional free radical polymerization processes. The novelty of the present polymerization is that the molecular weight of a polymer can be predefined by the initiator concentration which is independent of the monomer conversion unlike in a "living" free radical polymerization. In conclusion, a simple but novel photoinitiator has been identified for the controlled synthesis of PMMA with predefined molecular weights and narrow polydispersity through a photoinitiated free radical polymerization approach. This method would also facilitate the synthesis of "macroiniferters" with well-defined reactive end functional groups, useful for the designing of block copolymers by a *pseudo* "living" free radical mechanism. Detailed studies of polymerizations using MAX and similar photoinitiators and their use in controlled block and graft copolymer synthesis are in progress.

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CORRECTIONS

D. H. Gracias and G. A. Somorjai*: Continuum Force Microscopy Study of the Elastic Modulus, Hardness and Friction of Polyethylene and Polypropylene Surfaces. Volume 31, Number 3, February 24, 1998, p 1269−1276. Published on the Web January 28, 1998.

Equation 13 is a repetition of eq 11. The correct eq 13 is

$$F = \tau A = \tau\left[\frac{3\pi^{3/2}R}{4E^*}\left(W + 3\pi R\gamma + \sqrt{6\pi R\gamma W + (3\pi R\gamma)^2}\right)\right]^{2/3} \quad (13)$$

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