SHORT COMMUNICATIONS

Living Radical Polymerization of Methyl Methacrylate with a Tetrafunctional Photoiniferter: Synthesis of a Star Polymer

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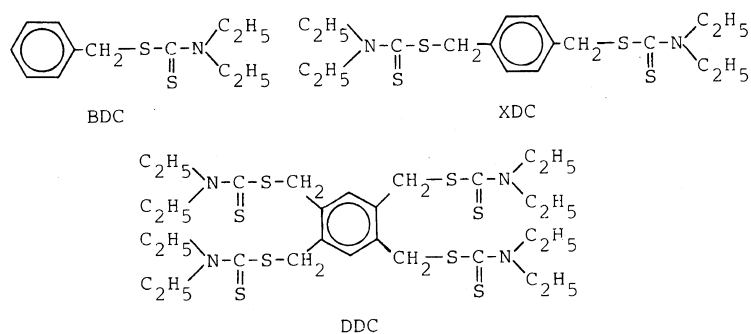*Osaka City University, Sugimoto, Sumiyoshi-ku,*
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In previous papers,[1,2] it has been reported that AB and ABA block copolymers are easily synthesized through living radical polymerizations using polymeric photoiniferters obtained from benzyl N,N-diethyldithiocarbamate (BDC) and p-xylylene bis(N,N-diethyldithiocarbamate) (XDC) as mono- and bi-functional photoiniferters. It was also noted that the living photopolymerizations took place with some organic sulfur compounds other than BDC and XDC.[1-5]

This technique was recently applied to the synthesis of a variety of block copolymers, AB and ABA types consisting of random and alternating copolymer seuqences,[6] and three or four component block copolymers.[7]

If 1,2,4,5-tetrakis(N,N-diethyldithiocarbamylmethyl)benzene (DDC) is used as a tetrafunctional photoiniferter, it is expected to give a star polymer. In this communication, the radical polymerization of methyl methacrylate (MMA) with DDC is described in comparison with that with BDC and XDC. The results of fractionation to confirm the formation of star polymers are also described.

EXPERIMENTAL

BDC and XDC were prepared according to the methods described previously.[1] DDC was prepared by the reaction of 1,2,4,5-tetrachloromethylbenzene with sodium N,N-diethyl-

dithiocarbamate in ethanol at room temperature for a day and recrystallized from a benzene/n-hexane mixture (ca. 1:1 by vol.); mp 125.5—126.3°C. DDC thus obtained was confirmed to be pure by elemental analysis, TLC, ^{13}C NMR and UV spectra. *Anal.* Found: S 35.50%, Calcd: S 35.46%; λ_{max} 252 nm (ε 44600) and 282 nm (44000) in chloroform. Monomers, solvents and other reagents were purified by the usual methods.

Photopolymerization of MMA was carried out in the presence of BDC, XDC, or DDC in benzene at 30°C under irradiation with a Toshiba SHL-100 UV lamp from a distance of 10 cm. After polymerization for a given time, the polymer was isolated by pouring the polymerization mixture into methanol. The polymers were purified by reprecipitating their benzene solutions into methanol three times, followed by drying in vacuum.

To isolate a star polymer, the polymer obtained was fractionated by the fractional precipitation method[8,9] in which acetone–water mixtures were used as solvent–precipitant systems. During this procedure, the temperature was kept constant at $30 \pm 0.05°C$. The polymer fractions separated were dried under reduced pressure, and their intrinsic viscosities ([η]) were determined in benzene at 30°C. The average-molecular weight ($\bar{M}$) of the polymers was calculated from [η] using the following equation.[10]

$$[\eta] = 6.27 \cdot 10^{-5} \, \bar{M}^{0.76}$$

UV spectra of the polymers were measured in acetonitrile with a Hitachi EPS-3T Recording Spectrophotometer. The number of the N,N-diethyldithiocarbamate groups [$(C_2H_5)_2NCSS-$] bonded to the PMMA chain end was approximately determined from the average-molecular weight and absorbance at 282 nm of the polymer, the latter being compared with that of methyl N,N-diethyldithiocarbamate.

RESULTS AND DISCUSSION

Figures 1 and 2 show the time–conversion and time–$\bar{M}$ relations, respectively, in the photopolymerizations of MMA with BDC, XDC, and DDC as mono-, bi- and tetrafunctional photoiniferters in which the concentration of the N,N-diethyldithiocarbamate group was kept constant: [BDC] = [XDC]/2 = [DDC]/4.

As evident in Figure 1, the time-conversion relations observed by all of these photoiniferters are identical to one another, *i.e.*, the polymer yields increase linearly with polymerization time. These results indicate that these three kinds of N,N-diethyldithiocarbamate groups show identical reactivity for radical polymerization.
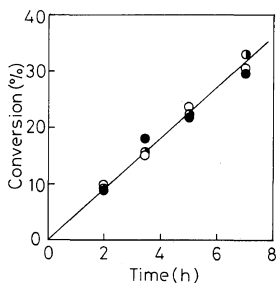
From Figure 2, the $\bar{M}$ values of the PMMA

Figure 1. Time–conversion relation in the photopolymerization of MMA with BDC, XDC, and DDC as photoiniferters in benzene at 30°C: [MMA] = 7.5 mol l^{-1} [BDC] = 5.4 · 10^{-4} mol l^{-1} (●); [XDC] = 2.6 · 10^{-4} mol l^{-1} (◐); [DDC] = 1.3 · 10^{-4} mol l^{-1} (○).
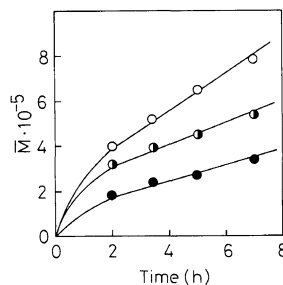

Figure 2. Time–$\bar{M}$ relation in the photopolymerization of MMA with BDC, XDC, and DDC as photoiniferters in benzene at 30°C. See Figure 1 for polymerization conditions: BDC, (●); XDC, (◐), DDC (○).

Table I. Fractionation of PMMA Obtained by DDC[a]

Fraction No.	Cumulative wt %	$\bar{M} \times 10^{-5}$	Number of end groups	
			From $\bar{M}$ and UV	From $\bar{M}/\bar{M}_0$[b]
1	4.32	19.5	5.2	5.8
2	11.11	14.0	4.8	4.2
3	18.04	13.5	4.5	4.0
4	20.54	11.0	3.9	3.3
5	23.97	10.8	2.6	3.2
6	39.64	7.75	2.3	2.3
7	44.30	7.65	1.8	2.3
8	48.02	7.32	1.7	2.2
9	59.57	6.21	1.5	1.8
10	62.62	5.55	—	1.6
11	70.82	5.55	1.1	1.6
12	75.08	3.70	—	1.1
13	82.51	3.07	1.0	0.9
14	89.75	2.68	—	—
15	93.80	1.97	1.1	—
16	97.85	0.93	—	—
17	100.00	0.65	2.1	—

[a] Polymerization was carried out in benzene at 30°C under irradiation of UV light from a distance of 10 cm; [MMA] = 7.5 mol l^{-1}, [DDC] = 1.3 × 10^{-4} mol l^{-1}, 7 h (yield 30%, $\bar{M} = 7.8 \cdot 10^5$).

[b] $\bar{M}_0 = 3.37 \times 10^5$ for PMMA obtained by BDC under similar conditions.

obtained are also observed to increase as a function of reaction time, indicating that these polymerizations proceed *via* a living radical mechanism.[1−4] The relative ratio of $\bar{M}$ was 1.0 : 1.7 : 2.5 for BDC, XDC, and DDC. If BDC, XDC, and DDC act as ideal photoiniferters, this ratio must be 1 : 2 : 4.

The fact that the relative $\bar{M}$ value observed for XDC was somewhat lower than 2.0 was in agreement with the result described in the previous paper.[1] This indicates the polymerizations of MMA by BDC and XDC do not proceed according to the ideal mono- and bifunctional mechanisms strictly, probably owing to self-termination as was pointed out in the biradical propagation of thermal polymerization.[11)] The low value may also be attributable to the uncertainty of the $\bar{M}$ values determined viscometrically.

Table I shows the results of fractionation of the PMMA obtained by DDC. In this table, the number of end groups was determined from $\bar{M}$ and UV absorption data (see Experimental) and also from the ratios $\bar{M}/\bar{M}_0$ in which $\bar{M}_0$ is the average-molecular weight of PMMA obtained by BDC under similar conditions. If the end groups show an equal reactivity (see Table I), the number of end groups can be determined by the ratio, $\bar{M}/\bar{M}_0$.

As can be seen from Table I, the numbers of N,N-diethyldithiocarbamate end groups per one polymer molecule obtained by both methods are quite similar and decrease with decreasing $\bar{M}$ of the polymer fractions. If the star polymer is assumed to have more than two end groups, the star polymer would be produced in a 39—48% yield. The star polymers were colorless powder materials and soluble in benzene, tetrahydrofuran, acetonitrile and chloroform.

These polymers were found to serve further as polyfunctional photoiniferters for the polymerization of St to give soluble star-type block copolymers which were then converted to gel-like polymers on prolonged photopolymerization. However, the polymers with functionalities less than 2.0 did not cause gelation, and gave soluble block copolymers.

More detailed results will be reported in a future publication.

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