Macromolecules **1994,** *27,* 3319–3321

Photochemical Control of Molecular Weight during Free-Radical Polymerization

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Received December 6, 1993; Revised Manuscript Received February 28, 1994[⊛]

ABSTRACT: Photolysis of 1,3-(di-1-naphthyl)propan-2-one (DNP) during the free-radical polymerization of vinyl monomers such as styrene and methyl methacrylate provides naphthylmethyl radicals which appear to terminate the growing chains in a nearly quantitative manner. The number-average molecular weight decreases with the amount of DNP used and is inversely proportional to the square root of the light intensity. This provides a means of controlling the molecular weight of polymers which is independent of other polymerization conditions. Furthermore, since each chain appears to be terminated with a fluorescent group, the number-average molecular weight of the polymer can be determined independently from a simple measurement of the fluorescence intensity per unit mass.

Introduction

The control of molecular weight during free-radical polymerization of vinyl monomers is important from both scientific and practical points of view. Since many properties of polymers depend on their molecular weights, methods of control are essential in industrial practice. In the absence of chain transfer, the number-average molecular weight, $\bar{M}_n$, is defined by the ratio of the rate of propagation to the rate of termination. Using the conventional description of free-radical polymerization kinetics

$$R_p = k_p[M][M^\bullet] \tag{1}$$

$$R_t = k_t[M^\bullet]^2 \tag{2}$$

and hence

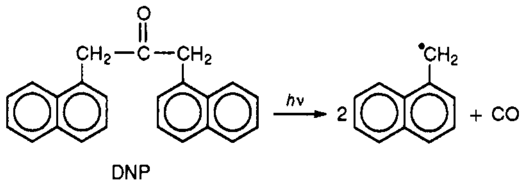
$$R_p/R_t = k_p[M]/k_t[M^\bullet] \tag{3}$$

where k_p and k_t are the rate constants for propagation and termination and [M] and $[M^\bullet]$ are the concentrations of monomer and growing radical species, respectively. Control of molecular weight can be achieved by increasing the free-radical concentration $[M^\bullet]$, but this also increases the rate of termination. In practice, only limited changes can be made by varying the temperature (due to different temperature coefficients of k_p, k_t, and k_i) since the overall rate of polymerization must be limited to maintain proper temperature control and reasonable rates of polymerization. In many cases molecular weight is controlled by addition of chain-transfer agents like mercaptans. In general, these do not affect the overall rate of polymerization since the termination of one chain leads to the initiation of another.

This paper describes a new method of controlling polymer molecular weight which is independent of other parameters of the copolymerization system, including temperature.

The compound 1,3-(di-1-naphthyl)propan-2-one (DNP) has been shown by Johnston and Scaiano[1] to photolyze by a "reluctant" Norrish type I reaction via the excited singlet state to give two naphthylmethyl radicals and carbon monoxide (Scheme 1). Although the quantum yield is low (<0.01), product analysis indicates that the only compounds formed are obtained by recombination of naphthylmethyl radicals with themselves or with radicals obtained by hydrogen abstraction from the solvent. The naphthylmethyl radicals are relatively stable toward hydrogen abstraction, so on irradiation of DNP in a solvent resistant to radical extraction, they would be expected to build up to a relatively high steady state approximately equal to

Scheme 1



$$[R^\bullet] = [(\phi_I I_A)/k_R]^{1/2} \tag{4}$$

where I_A is the light absorbed by DNP, ϕ_I is the quantum yield of photolysis, and k_R is the rate constant for recombination of naphthylmethyl radicals. Studies carried out by the same authors showed that at low light intensities the excited triplet played a negligible role in the photolysis, but at laser intensities similar products could be obtained by a two-photon process.

If DNP were present during a free-radical polymerization, on exposure to light absorbed by DNP most of the growing polymer chains might be expected to be terminated by naphthylmethyl radicals, even at low light intensities. The present studies were carried out to test this hypothesis.

Experimental Section

Synthesis of 1-Naphthaleneacetyl Chloride. In a two-necked round-bottom flask equipped with a rubber septum, glass stopper, and magnetic stirrer was placed 2 g (0.0107 mol) of 1-naphthaleneacetic acid (Aldrich) in 10 mL of dry benzene solution. To this mixture was added 20 mL of thionyl chloride, and the mixture was stirred for 6 h at room temperature. The solvents were removed under vacuum to give 1-naphthaleneacetyl chloride as an oily solid which was stored in an air-tight container for future use.

Synthesis of (1-Naphthylmethyl)magnesium Chloride. 1-(Chloromethyl)naphthalene (2.0 g, 0.0113 mol, Aldrich) was dissolved in 20 mL of dry ether. This solution was slowly added via a gas-tight syringe to a round-bottom flask (equipped with a condenser, nitrogen inlet, and magnetic stirrer) containing 1.0

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[⊛] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

0024-9297/94/2227-3319$04.50/0 © 1994 American Chemical Society

Table 1. Polymerization Conditions

run no.	benzene (g)	AIBN (mg)	styrene (g)	ketone (mg)	time (h)	temp (°C)	light intensity (W/cm^2)	polymer yield (g)	conversion (%)	$\bar{M}_n$ GPC	$\bar{M}_n$ ebulliometry	$\bar{M}_n$ fluorescence	$\bar{M}_w/\bar{M}_n$
A1	2.3	4.7	3.0	8.9	7.0	50	0	2.0	67	78 000			1.83
A2	2.3	4.7	3.0	8.9	7.0	50	2.20	1.20	41	56 500		55 580	1.55
A3	2.3	4.7	3.0	8.9	7.0	50	6.00	1.18	39	40 500		38 050	1.62
A4	2.3	4.7	3.0	8.9	7.0	50	12.00	1.15	38	26 300	25 600	24 320	1.76
A5	2.3	4.7	3.0	8.9	7.0	50	16.00	1.08	36	17 500	16 500	16 870	2.16
B1	4.0	8.0	4.0	2.38	5.5	60	16.00	0.85	21	26 900	26 700	26 440	1.66
B2	4.0	8.0	4.0	5.13	5.5	60	16.00	0.80	20	24 800	24 000	24 840	1.73
B3	4.0	8.0	4.0	8.19	5.5	60	16.00	0.80	20	19 200	21 100	20 000	1.91

g of activated magnesium metal pieces at 0 °C. The reaction mixture was stirred continuously for 30 min. The Grignard reagent thus prepared was stored under nitrogen at 0 °C and was utilized immediately for further reaction.

Synthesis of DNP. 1-Naphthaleneacetyl chloride (2.0 g, 0.0098 mol) was dissolved in 20 mL of dry ether. The solution was transferred to a three-necked round-bottom flask equipped with a nitrogen inlet, magnetic stirrer, and rubber septum. The reaction mixture was cooled to −78 °C by an acetone/dry ice bath. To this cooled solution, the solution of Grignard reagent prepared previously was added dropwise over 20 min via a gas-tight syringe. The reaction mixture was stirred at low temperature for 20 min and then warmed to room temperature over a 60-min period. The reaction was quenched by adding 2 mL of distilled water and was transferred to a separatory funnel and washed with distilled water, then with a 2% NaOH solution, and again with distilled water. The washed ethereal solution was dried over $MgSO_4$, and the solvent was removed under vacuum to give the crude product, which was purified over a short silica gel column (70–30 mixture of dichloromethane–hexane) to give 0.5 g (25% yield) of DNP as a yellow crystalline solid. IR: 1730 cm^{-1} (C=O); 200-MHz ^{1}H NMR: δ 8.1–6.98 (m, 14H, aromatics), 4.08 (s, 4H, CH_2); mass spectrum: 310 M$^+$, 141.

Polymerization of Styrene. The conditions for the thermal polymerization of styrene are summarized in Table 1. The reaction was initiated by thermal decomposition of AIBN at 50–60 °C, while the terminating naphthylmethyl radicals were generated by photolysis of DNP at various light intensities. The reaction mixture was purged with nitrogen for 10 min and transferred to a quartz polymerization cell (2 in. × 1 in.) equipped with a nitrogen inlet and heating jacket. The polymerization cell was mounted on an optical bench in front of a medium-pressure Hg lamp (250 W, GEC). The polymerization was carried out under N_2, while the temperature was maintained constant by a circulating-water bath. The light was collimated with a quartz lens, and filters were used to control wavelength and intensity. The irradiation wavelength employed in each run was >320 nm. The light intensities were altered using quartz neutral-density filters (Opticon, 10, 30, 50, and 90% light transmittance). Absolute intensities were measured with a pyroelectric radiometer. Four runs were carried out while maintaining a constant monomer concentration and varying only the light intensity.

An additional series of polymerizations was carried out to determine the effect of DNP concentration. Benzene (4 g, 0.0513 mol), AIBN initiator (0.008 g), and a variable amount of DNP were added to styrene monomer. The polymers so obtained were purified by dissolving in benzene and reprecipitating twice from methyl alcohol. The samples were dried and stored in the dark. Polymerization data are shown in Table 1.

Gel Permeation Chromatography (GPC). The molecular weight measurements of the polymer samples synthesized were carried out using a Waters GPC equipped with two DuPont bimodal SEC type columns, a Waters 410 computerized differential refractive index (DRI) detector, and an Applied Biosystems programmable fluorescence detector. Exactly 70 μL of dilute polymer solution of known concentration was injected into the GPC instrument using tetrahydrofuran (THF) as eluant. Both DRI and fluorescence detector responses were recorded using an IBM-compatible personal computer. The naphthalene chromophores were excited at 300 nm and their emission was observed at wavelength >345 nm. Five narrow molecular weight distribution polystyrene samples were used to obtain a calibration curve of molecular weight vs elution volume.

Measurement of $\bar{M}_n$ by Fluorescence. Measurement of $\bar{M}_n$ by fluorescence required the determination of the response of both the DRI and fluorescence detectors. The data so obtained were used with the integrated area of the response from each detector. The fluorescence detector was precalibrated by injecting known concentrations of a standard solution of 1-methylnaphthalene in THF and recording the response in terms of area of fluorescence at the same excitation and emission wavelengths employed for the polymer samples. The slope of this calibration curve was utilized in the estimation of $\bar{M}_n$ by fluorescence.

Measurement of $\bar{M}_n$ by Ebulliometry. The number-average molecular weight of the polymers was also checked using a high-precision ebulliometer designed by H. X. Huber,[2] consisting of a pair of matched 60 junction thermopiles. The instrument is capable of determination of absolute molecular weights up to about 50 000.

Results and Discussion

The UV absorption spectrum of DNP is shown in Figure 1. In these experiments, a 320-nm cutoff filter was used, which means that most of the absorbed light was the mercury line at 356 nm. At this wavelength the absorbance of DNP is such that the light should penetrate at least 2 cm of solution at the concentrations used (Figure 1). Styrene, methyl methacrylate, and solvent benzene have negligible absorbances at 356 nm.

At low light intensities DNP photolyzes from the excited singlet prior to intersystem crossing to the triplet. The quantum yields are low, of the order of 0.01, but still sufficient to provide a source of stable naphthylmethyl radicals. Because of the low rate of hydrogen abstraction during photolysis, the steady-state concentration of naphthylmethyl radicals could easily exceed that of any other species by several orders of magnitude, thus ensuring nearly quantitative termination of all polymer chains.

Experimental results on the molecular weights of the polymers are consistent with this hypothesis. The data from experiments in which the photolysis light intensity was varied are shown in Table 1. GPC curves for samples A1, A2, and A4 are shown in Figure 2. The fluorescence detector shows no response for the control sample A1 but increasing response for A2 and A4 as the light intensity increases. The low molecular weight peak at $M \sim 1000$ not detected by the RI detector appears to represent a low concentration of highly fluorescent oligomers of unknown structure. The good agreement between the number-average molecular weights calculated from fluorescence and those from GPC and ebulliometry indicates that nearly quantitative termination by naphthylmethyl radicals is occurring.

A simple kinetic treatment of the photolysis data suggests the steady-state concentration of naphthylmethyl radicals should be proportional to the square root of the light intensity (eq 4). Since the rate of termination is proportional to [R$^\bullet$] the number-average molecular weight should vary inversely as $I^{1/2}$. A plot of this form from the data in Table 1 confirms the validity of the relationship at higher light intensities (Figure 3).

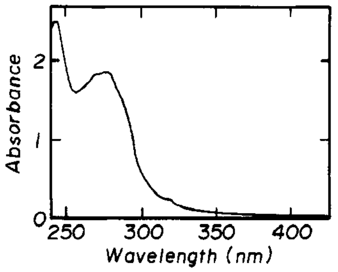

Figure 1. UV absorption spectrum of 1,3-(di-1-naphthyl)propan-2-one (3.51×10^{-5} M in methylene chloride).

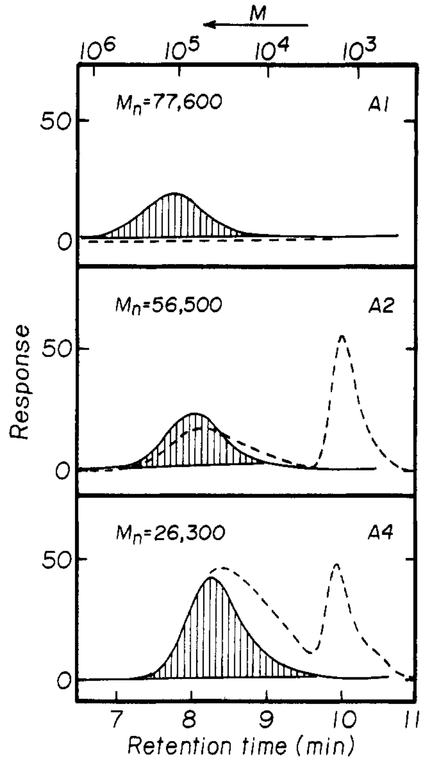

Figure 2. GPC curves from end-labeled polymer samples: A1 (no light); A2 (2.2 W cm^{-2}); A4 (12.0 W cm^{-2}). Refractive index detector is solid line and shaded area; dashed line is fluorescence detector.

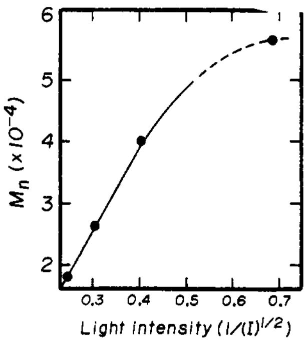

Figure 3. Variation of number-average molecular weight as a function of $I^{-1/2}$, where I is the light intensity (W cm^{-2}) reaching the front face of the polymerization reaction cell.

The result of changing the concentration of DNP is also shown in Table 1. Clearly, changing the light intensity is more effective than changing the concentration of terminator, but again there is strong evidence for quantitative termination of the growing polymer chains.

The process also works with methyl methacrylate. Figure 4 shows GPC results on poly(methyl methacrylate) made in a continuous polymerization reactor consisting of an 8-mm-i.d. Pyrex tube heated with a Pyrex water jacket and exposed to UV light from two mercury vapor lamps.

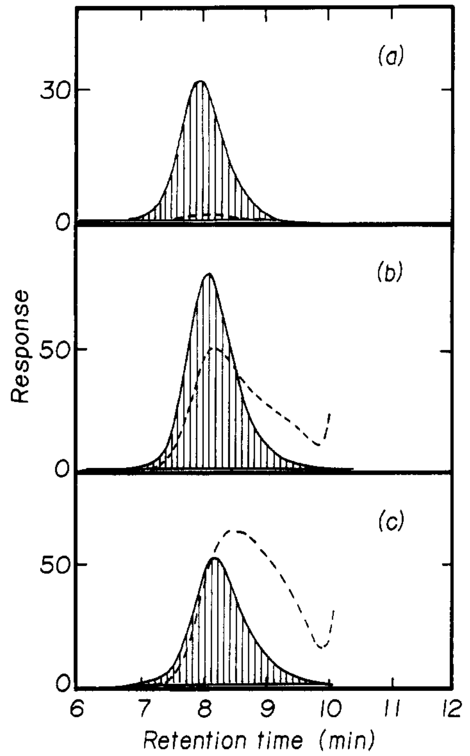

Figure 4. GPC traces for PMMA samples: (—) RI detector; (- - -) fluorescence detector. (a) Control (no light); (b) lamp distance 40 cm; (c) lamp distance 3 cm. Prepared by continuous polymerization in benzene solution at 86 °C.

The reaction mixture consisted of 60 wt % MMA monomer and 40% benzene containing 0.2 mol % lauroyl peroxide and 0.2 mol % DNP. The flow rate was 0.9 g min^{-1}, giving a residence time of ca. 10 min. The polymerization was carried out at 86 °C and the light intensity was varied by moving the position of the lamps. The conversion to polymer was <1% (~250 mg) even in the control sample, but labeling occurred across the entire molecular weight range, even at the lowest light intensity, as shown in Figure 4.

In summary, we have shown that the photolysis of DNP gives rise to naphthylmethyl radicals capable of terminating growing polymer chains during free-radical-initiated polymerization of styrene and MMA. This provides a method of independent control of the termination process in vinyl polymerization. The technique has several possible applications. (1) Since each chain appears to be terminated quantitatively, inclusion of a functional group such as ester, carboxylic acid, or alcohol in the terminator structure would allow efficient functionalization of polymer end groups. (2) In principle, any desired molecular weight distribution can be synthesized by programming the light intensity. (3) Runaway polymerization reactions such as those occurring in the "gel effect" region might be terminated with high-intensity light flashes.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for generous financial support and David Gravett and Sergio Paone for helpful discussions.

References and Notes

(1) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 5487.
(2) Smith, P.; Huber, H. X.; Guillet, J. E., manuscript in preparation.