

Pilot Plant Synthesis of Methacrylate Copolymer Precursors to Nonlinear Optical Materials

H. E. KATZ, M. P. BOHRER, D. A. MIXON, J. ALONZO,[†]
J. MARKHAM, J. E. SOHN, and D. I. COX,[†] *AT&T Bell Laboratories,
Murray Hill, New Jersey 07974*

Synopsis

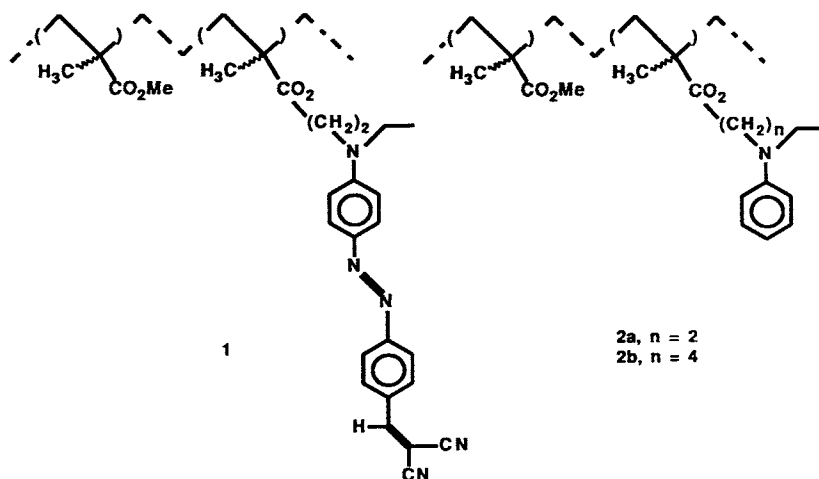
The copolymerization of methyl methacrylate with methacrylates containing anilino side chains was investigated. Azobis(isobutyronitrile) was a better initiator than benzoyl peroxide. Continuous feed of initiator was advantageous compared to adding the initiator all at once. The reaction was scaled up using a 10-L reactor, ultimately yielding hundreds of grams of the desired copolymers, which are valuable precursors to polymeric dyes used in nonlinear optical studies.

INTRODUCTION

Polymeric materials are promising for nonlinear optics applications.¹ We have demonstrated that solutions of dipolar azo dyes in thin films of amorphous polymers that have been electric field poled possess large second-harmonic and electrooptic coefficients.² As an extension of our initial efforts, we have recently begun to explore materials in which the dyes are covalently bound to polymer backbones.³ One predicted benefit of this approach is an increase in the stability of the polarization imparted by poling. Indeed, nonlinear optical coefficients for poled films of a random copolymer of structure **1** were much more stable than those for films of an analogous dye dissolved in poly(methyl methacrylate) (PMMA). In addition to the increased stability, advantages of dye copolymers over dye-polymer solutions include the potentially higher achievable concentration of active moieties without phase separation and the avoidance of mixing steps in the processing of the materials. The "saturation point" for solutions of dyes such as Disperse Red 1 in PMMA is 15–20 wt %.⁴ Macroscopic phase separation is not observed in copolymers such as **1** even at much higher concentrations of dye residue, although microscopic aggregation probably occurs at some point. Other polymers with attached nonlinear optical functionalities are under investigation in several other laboratories as well.⁵

Polymers of general structure **1** have been synthesized by azo coupling of dicyanovinylphenyldiazonium hexafluorophosphate to the anilino copolymer precursor **2a**.⁶ This method avoids the need to carry out radical polymerizations in the presence of potentially reactive⁷ dicyanovinyl functionalities and also makes possible the direct comparison of nonlinear optical properties arising from various azoacceptor groups attached to anilino polymer from a single

[†] AT&T Bell Laboratories Summer Research Program participants, 1987–1988.



Scheme 1.

batch. As interest in these materials for device fabrication has grown, it has become desirable to prepare 100-g quantities of **2a**. We have therefore examined the large-scale copolymerization of the constituent monomers methyl methacrylate (MMA) and **3**. This article reports the results of this investigation as well as the pilot plant scale-up of the synthesis of **2a**, from which adequate quantities are now available.

RESULTS AND DISCUSSION

Copolymers of MMA and **3** have been synthesized incorporating various proportions of the monomers. The alternative monomer **4** has also been employed in some polymerizations, yielding **2b**, which may be useful in assessing the effect of side chain length on the mobility of attached chromophores. Copolymers that we have prepared and characterized are listed in Table I, along with weight-average molecular weights (M_w) and glass transition temperatures (T_g). Although homopolymers of monomers such as **3** and **4** are known,⁸ their MMA copolymers have not been previously reported. The trend in T_g is as expected, with values intermediate between the T_g of PMMA (105°C)⁹ and the homopolymer of **3** (38°C)⁸ for polymers in the 10^4 – 10^5 M_w range.

TABLE I
 Copolymers of **3** and MMA

Mol % incorporation of 3	$M_w \times 10^{-3}$	T_g (°C)
5	19	
13	29	92
17	35	84
42	27	75
15 (of 4)	24	82

Preparations of 5 : 1 MMA : anilino methacrylate copolymers were performed under a variety of conditions, as summarized in Table II. Both **3** and **4** participated effectively in the polymerization (runs 1 and 2). The yield was considerably higher when initiator was maintained at a finite concentration throughout the reaction by constant addition (runs 2–5). Azobis(isobutyronitrile) (AIBN) is a superior initiator compared to benzoyl peroxide (BPO) in this system (run 4); unproductive decomposition of BPO may be induced by impurities in the aniline monomers, or conceivably by the monomers themselves. Values of M_w changed little from run to run at constant initial concentration of monomer; however, as expected, the molecular weight did rise when the monomer concentration was significantly increased and the initiator concentration was decreased (runs 6 and 7).

Three batches of **2a** were obtained from pilot plant reactions as described in Table III. Higher yields were obtained by continuously feeding initiator into the reaction mixture as opposed to employing only a small initial charge. By successfully executing these large-scale experiments, we have obtained hundreds of grams of **2a** for conversion to polymeric azo dyes and also demonstrated the

 TABLE II
 Preparation of Methyl Methacrylate Copolymers Incorporating 15–20 mol %
 Anilino Methacrylate Monomer^a

Run	Type	Initiator meq/eq monomer	Addition ^b	Changes ^a	% Yield	$M_w \times 10^{-3}$
1	BPO	4.6	A	None	26	26
2	BPO	7.7	A	Aniline monomer 4	30	20
3	BPO	21	B	Aniline monomer 4	45	21
4	AIBN	6.1	A	None	22 ^c	10
5	AIBN	12	B	None	51	15
6	AIBN	1.5	A	Concentration 1.6M	72	56
7	AIBN	1.5	A	Concentration 1.6M, Temperature 60°C	62	71

^a In MEK at reflux, aniline monomer is **3**, concentration is 0.3M in total monomer unless otherwise indicated.

^b A = all added at start, B = 10% added at start, the rest over 10–15 h.

^c Very small scale; a control with BPO under identical conditions gave 11% recovery.

TABLE III
 Pilot Plant Synthesis of 2

Moles MMA	Moles 3 ^a	Type	Initiator		% Yield	$M_w \times 10^{-3}$
			Initial amount (mol)	Added amount (mol)		
2.0	0.45	BPO	0.011	none	12	26
2.2	0.50	BPO	0.011	0.054	36	16
3.0	0.20	AIBN	0.003	0.021	65	19

^a Calculated as though 3 were pure; in fact, the purity was only ca. 70%.

feasibility of scaling up the polymerization in the event that the industrial-scale production of 2a becomes desirable.

EXPERIMENTAL

Solvents and reagents were used as received except as noted. Inhibitor was removed from MMA for bench-scale experiments by treatment with NaBH₄ followed by elution through basic alumina, and for pilot plant runs by distillation. Monomer 3⁸ was synthesized by esterification of *N*-ethyl-*N*-hydroxyethyl-aniline with methacryloyl chloride in anhydrous tetrahydrofuran (THF) in the presence of triethylamine at 0°C. The product was isolated by extractive workup from ether and aqueous NaHCO₃ and elution through neutral alumina with hexane-dichloromethane. The product contained 20% of a previously observed,¹⁰ unidentified impurity that caused an accordingly lower fractional incorporation of 3 into 2a as determined by integration of proton NMR spectra. Otherwise, the proportions of the two monomer residues in copolymer products were the same as the monomer ratios in the reaction mixture. Compound 4¹¹ was prepared in three steps from *N*-methylaniline by successive treatment with succinic anhydride, borane in THF, and methacryloyl chloride. Proton NMR spectra were recorded on a Bruker 360-MHz instrument, molecular weights were obtained by gel permeation chromatography relative to PMMA standards, and glass transition temperatures were determined using a DuPont 1090 Differential Scanning Calorimeter. The T_g 's reported are the temperatures at the maximum slopes of the plots of heat capacity vs. temperature.

Copolymer of MMA and Anilino Methacrylate (Bench Scale)

To a round-bottom flask were added monomers, solvent, and the initial charge of initiator. The resulting solution was purged with argon and then stirred at reflux under argon while additional initiator, if any, was added. After 20 h, the mixture was allowed to cool, and then was poured into 4 volumes of stirred hexane. The supernatant liquid was decanted, and the gummy residue was redissolved in methyl ethyl ketone (MEK) and reprecipitated from 6 volumes of hexane and collected as a white powder. ¹H NMR (CDCl₃, of 2a, vs. Me₄Si) δ 0.8–1.3 (m, backbone CH₂ and aniline CH₃), 1.8–2.0 (b, backbone CH₃), 3.4

(MeCH₂N), 3.6 (OCH₃ and CH₂N), 4.1 (CH₂O), 6.7 (*o*- and *p*-ArH), 7.2 (M-ArH). The NCH₃ signal in the NMR spectrum of **2b** appeared at 3.0 ppm.

Pilot Plant Synthesis of **2a**

MMA and **3** were added to a glass-and-Teflon reactor containing 10 L of MEK. The solution was deoxygenated and heated to 80°C. The initial charge of initiator was added and the polymerization proceeded with stirring under a positive pressure of nitrogen. Additional initiator was continuously fed as a solution in 450 mL of MEK at the rate of 30 mL/h. After 18 h, the reaction mixture was transferred under pressure into a chilled vessel. When the solution temperature had dropped below 30°C, the solution was transferred into a stirred stainless steel tank containing 40 L of hexane. When this transfer was complete, the stirring was halted and the solids allowed to settle over several hours. The supernatant liquid was removed by pressure-assisted siphoning, 2 L of MEK was added to the residue, and the steel tank was sealed. After 24 h, the residue, softened by diffused solvent vapors, had completely flowed into the solvent pool and formed a solution of crude **2a**. This solution was harvested via a spigot at the bottom of the tank and precipitated portionwise into a total of 12 L of hexane. The precipitate formed a hard crust that was allowed to dry in air over several days. The copolymer obtained in this manner was essentially identical to that that had been prepared on smaller scales, as determined by NMR, physical properties, and subsequent chemical reactivity.

We are grateful to D. Fish and H. M. Gordon for assistance in characterizing the polymers.

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Received February 17, 1989

Accepted June 21, 1989