

Catalytic Chain Transfer in Polymerization of Methyl Methacrylate. II. Continuous Synthesis and Purification of Macromer*

K. G. SUDDABY, R. AMIN SANAYEI, A. RUDIN, and K. F. O'DRISCOLL†

The Institute for Polymer Research, University of Waterloo, Waterloo, Ontario, Canada

SYNOPSIS

A continuous process for the production of kilogram quantities of poly(methyl methacrylate) macromers using catalytic chain transfer agents is described. The macromers are synthesized in a tubular reactor and isolated from unreacted monomer using a twin-screw extruder. Three concentrations of catalytic chain transfer agent were used and macromers of $M_n = 480, 752, \text{ and } 1334$ were made. The behavior of the tubular reactor runs over time was determined by monitoring both conversion and the molecular weight distribution of the macromers in the reactor effluent. Trends in this behavior with respect to time and catalytic chain transfer agent concentration are discussed. Experimental details are given and the efficiency of the devolatilization of the monomer from the reactor effluent using a twin-screw extruder is examined.

INTRODUCTION

In recent years, there has been a great deal of work done on the synthesis and polymerization of macromers.¹⁻¹⁰ The interest in macromers stems from their utility in the preparation of well-defined graft copolymers. This paper describes the details of a recent study in which a continuous process for the synthesis and isolation of kilogram quantities of methyl methacrylate macromers was developed. Subsequent characterization of the resultant macromers showed that these polymerizations could be adequately described by using classical kinetics and assuming plug flow behavior.

Poly(methyl methacrylate) (PMMA) macromers of high purity were produced in the bulk free radical polymerization of methyl methacrylate (MMA) through the use of a catalytic chain transfer agent (CCTA).¹¹⁻¹⁴ Introduction of CCTAs to a free radical polymerization results in a low molecular weight polymer containing a single-terminal unsaturation

per molecule. The structure of the resultant macromer is illustrated in Figure 1.

A tubular reactor was used for this polymerization. The use of tubular reactors in commercial polymerization reactions has been limited by thermal and flow instabilities resulting from the coupling of the viscous nature of polymers with the exothermic nature of their formation.¹⁵⁻¹⁷ Recent work¹⁷ has, however, defined the operating conditions in which tubular reactors may be useful for the synthesis of polymers under continuous operation. The polymerizations discussed here were operated within these conditions, i.e., low molecular weight polymer was produced at moderate conversion. This allowed the reactor to achieve and maintain a steady state without the occurrence of fouling.

The macromers were isolated from unreacted monomer in the reactor effluent by a continuous devolatilization process using a twin-screw extruder. The devolatilization of polymeric products is an important unit operation and has been studied in some detail.^{18,19} These studies have shown that this process can be divided into two distinct regimes: the flash evaporation regime and the diffusion-controlled regime. In the former, the rate of devolatilization becomes limited by the rate at which heat transfer can replace the latent heat of vaporization

* Part I is Ref. 13.

† To whom correspondence should be addressed.

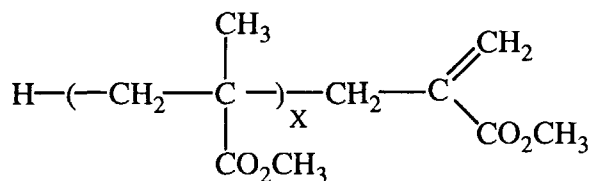


Figure 1 Structure of PMMA macromers.

of the volatiles, and in the latter, the devolatilization rate depends strongly on the rate at which new surface area can be generated.

EXPERIMENTAL

CCTA Synthesis

The CCTA used in this study was the boron fluoride derivative of cobaloxime (COBF) (Fig. 2). It is extremely effective as a chain transfer agent,¹³ having a chain transfer constant for MMA of 10^4 and, as a result, can be used in very low concentrations. It was synthesized and its activity was measured following methods described in Ref. 13.

Macromer Synthesis

The monomer, MMA, and initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN) were obtained from Aldrich and Polysciences, respectively, and were used without further purification.

The tubular reactor used was a water-jacketed glass reactor with an internal diameter of 21.5 mm and wall thickness of 1.6 mm. It was 1.75 m long and contained a volume of 635 mL. To minimize dead volume due to evolved gases, it was operated in a vertical geometry with the feed entering the bottom. Use of this vertical geometry has also been shown to provide a larger range of feasible operating conditions for continuous polymerization in a tubular reactor.²⁰

Reactor feed solutions for three runs with different COBF concentrations were prepared by stirring COBF and ADVN into monomer deoxygenated by nitrogen bubbling. These solutions (7 kg each) contained 0.0025 M ADVN and 50, 25, or 12.5 ppm COBF.

The reactor feed was controlled by a fluid metering pump calibrated to deliver 0.861 mL/s (resulting in a 737.5 s mean residence time). Throughout the polymerization, the water circulating through the jacket was maintained at 86°C. Sampling of the reactor effluent occurred over eight residence times,

at specified intervals between 0 and 100 min, to examine the tubular reactor's behavior over time. Time 0 was defined as the emergence of the first product from the top of the reactor. The reactor effluent samples were characterized for conversion by gravimetry and for molecular weight by both GPC and proton NMR. The remaining reactor effluent was chilled, inhibited (0.1 g *p*-methoxyphenol), and stored at -10°C .

The macromer and unreacted monomer in the reactor effluent were separated by devolatilization on a Leistritz L30.34 twin-screw (see Fig. 3). The extruder was set up with seven zones, not including the die outlet. A fully intermeshing, counter-rotating, self-wiping screw geometry was used. The screw was arranged so that the pitch in zones 1–5 was 6 mm (per rotation), and in zones 6 and 7, 20 mm. The screw speed was 50 rpm. The temperature settings for the various zones (with zone 8 representing the die) are listed in Table I. The temperatures in zones 6 and 7 were controlled to give the product a suitable extrusion viscosity.

During start up, the die was empty so the system would not hold a vacuum and efficient devolatilization was prevented. To overcome this, the die was plugged with a bolt until macromer sufficient to form a seal built up at the die. This stage was evident by the increased current drawn by the extruder motor as it tried to convey macromer through the plugged die. Once this seal was formed, the bolt was removed and the extruder feed rate was matched to the rate of devolatilization so that a steady state was achieved.

The feed port was placed in zone 2, and viewing ports were placed in zones 1, 3, and 6. Vacuum ports were placed in zones 1 and 3, and the vacuum pump was set so that the gauge read 600 Torr of vacuum. A chiller and a collection vessel were placed between the vacuum ports and the vacuum pump to recover monomer. This arrangement of the vacuum ports

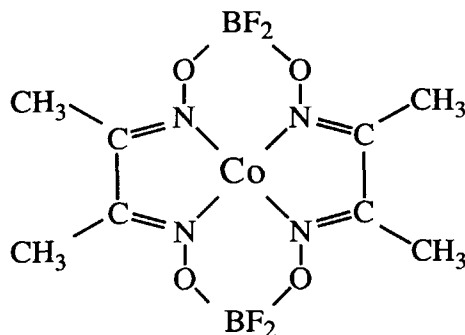


Figure 2 Structure of cobaloxime boron fluoride.

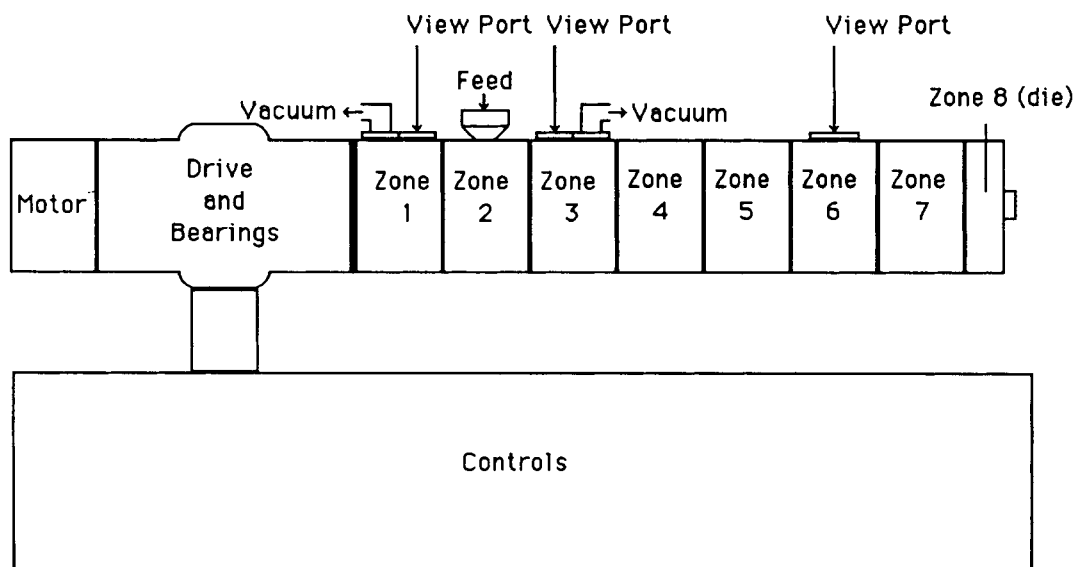


Figure 3 Schematic of the twin-screw extruder configuration.

around the feed port enabled the high monomer content solution (85% monomer in the feed) to be confined in the first few zones where flash evaporation occurred. This high monomer content solution was not viscous enough to be conveyed forward by the screw and so remained in the vicinity of the feed port. However, as monomer was removed, macromer-rich portions of the solution with their increased viscosity began to stick to the screw and were transported along the barrel. Once sufficient monomer had been removed from the solution to allow it to be conveyed by the screw, the devolatilization was beginning to become diffusion controlled. The removal of monomer in the flash evaporation stage was, however, the rate-limiting process resulting in the viscous product only partially filling the barrel, leaving the remainder of the barrel under vacuum. As the viscous melt was conveyed along the barrel, its surface was constantly being renewed and exposed to vacuum, thus enhancing the rate of diffusion-controlled devolatilization. This resulted in macromer products that were collected from the die and analyzed for residual monomer and molecular weight by NMR.

Product Characterization

The low molecular weight of the macromers required care to determine conversion gravimetrically. Weighed quantities of the samples were initially dried under a stream of air at room temperature. The dried samples were then placed in a vacuum oven for 12 h and heated, to 40°C for the 50 ppm

run or to 60°C for the 25 and 12.5 ppm runs. Conversion was then determined by the weight of these samples corrected for residual monomer.

Proton NMR was used to analyze the dried samples for both their molecular weight and their residual monomer content. A Bruker AC 300 FT-NMR spectrometer was used to obtain quantitative spectra at 30°C using CDCl_3 as both the solvent and the internal reference (7.24 ppm relative to TMS). A typical spectrum is shown in Figure 4. The mol fraction of residual monomer was determined by the ratio of the area of the monomer vinyl proton peak (at 6.1 ppm) to that of the vinyl peak due to macro-

Table I Extruder Temperature Settings for Devolatilization

Zone	Run A	Run B	Run C
	[COBF]		
	25.0 ppm	50.0 ppm	12.5 ppm
	T (°C)	T (°C)	T (°C)
1	80	90	100
2	80	90	100
3	80	90	100
4	95	90	95
5	80	80	80
6	80	20	80
7	10	-10	80
8	25	20	80

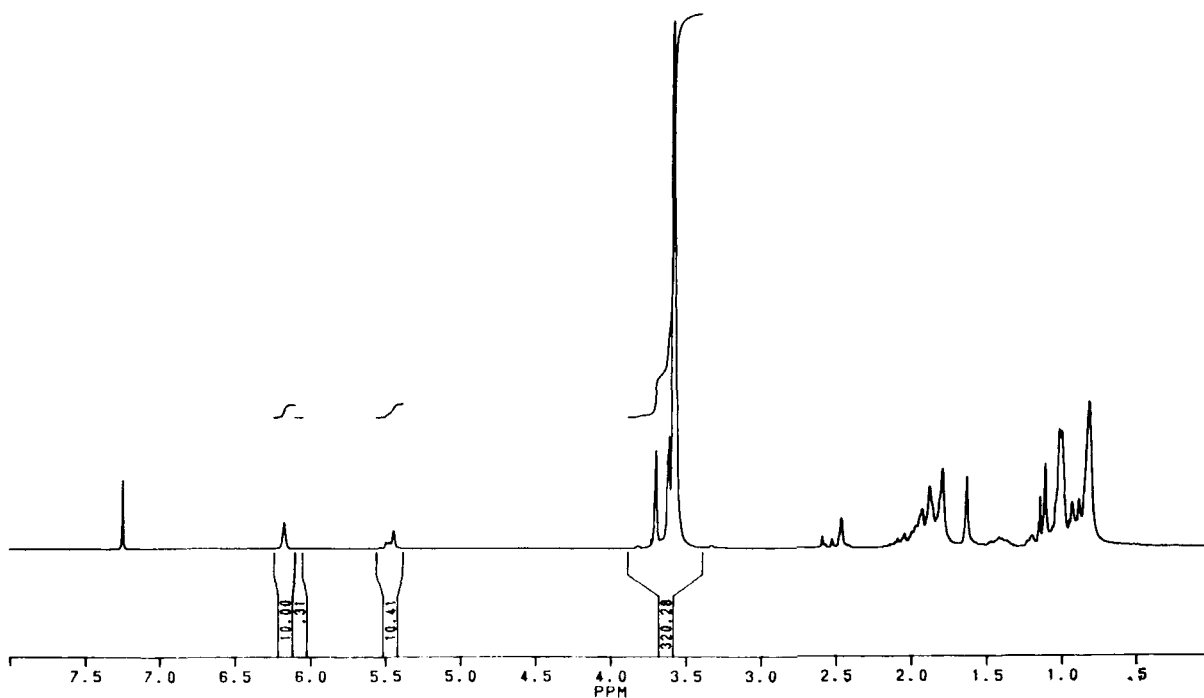


Figure 4 A typical ^1H spectrum of PMMA macromer. Sample prepared with 12.5 ppm COBF taken to 14.1% conversion.

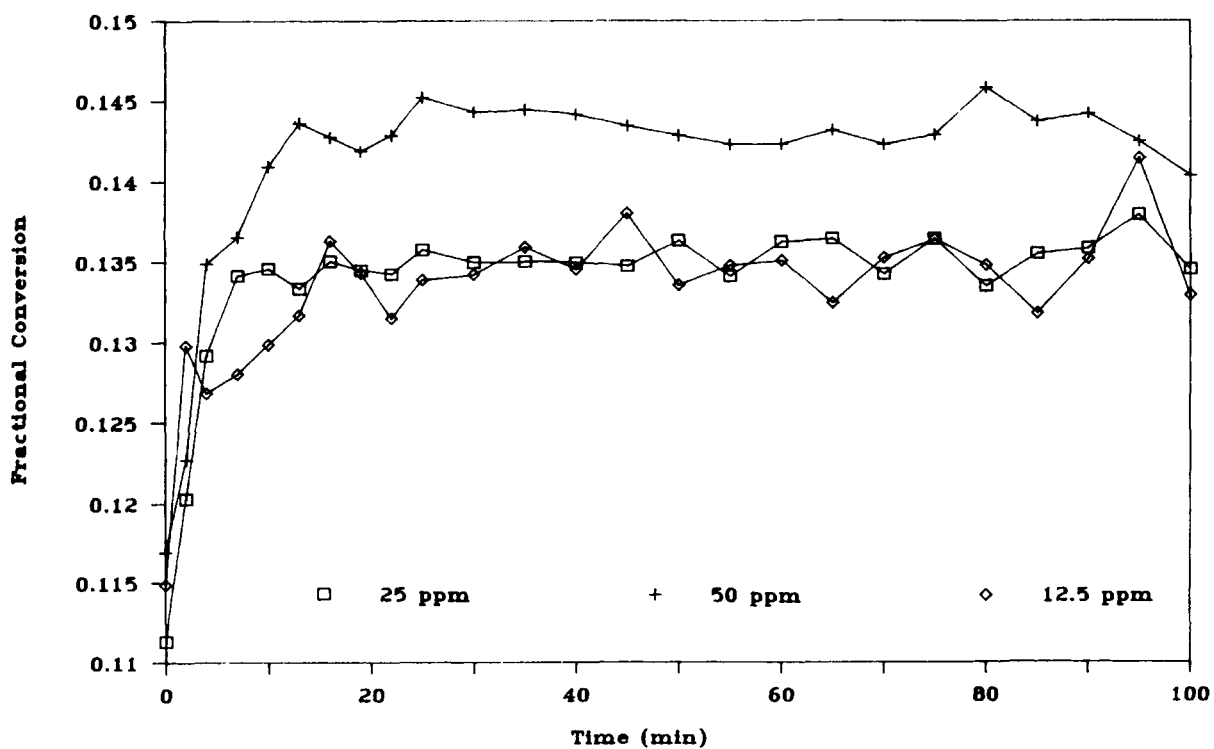


Figure 5 Conversion vs. time plot for PMMA macromer tubular reactor runs.

Table II PMMA Macromer Tubular Reactor Runs Number Average Molecular Weight

Time (min)	Method											
	Run A [COBF] (25.0 ppm)				Run B [COBF] (50.0 ppm)				Run C [COBF] (12.5 ppm)			
	NMR	3 DRI	3 UV	M DRI	NMR	3 DRI	3 UV	M DRI	NMR	3 DRI	3 UV	M DRI
0	1095	1129	1197	1043	581	569	576	580	2781	1967	2060	1670
2	841	903	934	855	507	503	517	514	1640	1660	1707	1492
4	763	814	812		508	502	512		1398	1409	1598	
7	747	727	725	700	468	457	473	475	1250	1335	1338	1201
10	720	707	718		465	419	423		1261	1155	870	
13	633	681	735		470	430	450		1219	1189	1172	
16	683	709	717		458	441	454		1166	1165	1112	
19	703	701	707		461	432	450		1141	1161	1145	
22	620	669	673		447	432	450		1130	1173	1175	
25	723	702	710	687	454	450	470	462	1203	1150	1114	1020
30	697				448				1160			
35	699				462				1175			
40	692	692	706		459	438	465		1103	1191	1175	
45	699				463				1135			
50	718				456				1146			
55	694				399				1143			
60	697	673	678		446	427	450		1183	1098	1068	
65	690				447				1170			
70	697				461				1081			
75	727				454				1078			
80	709	691	695		455	441	463		1123	1090	1046	
85	703				463				1109			
90	716				456				1068			
95	668				459				1071			
100	719	674	681		456	428	456	459	1078	1110	1081	1005
Avg 22-100 min	698	684	691	687	452	436	459	461	1127	1135	1110	1013

[Mo] = 9.39M; [Io] = 0.00250M.

mer (at 6.2 ppm). The number average molecular weight of the macromer was determined by taking the ratio of the area (corrected for monomer) under the OCH₃ peaks (3.6 ppm) to that of the macromer vinyl peaks (5.5 and 6.2 ppm). Since each macromer has a single-terminal double bond (Fig. 1), the molecular weight may be determined. Knowing this and the mol fraction residual monomer, the weight fraction of residual monomer can be determined.

Gel permeation chromatography was used to determine the molecular weight distributions of the PMMA macromer from selected samples. These measurements were performed, using THF as the eluent, on a unit equipped with computer-interfaced DRI and UV (254 nm cutoff filter) detectors. The system was operated with either a Jordi-gel 410/E206,207 mixed-bed column or 3 PL-gel columns with 1000, 500, and 100 Å pore sizes. Both polysty-

rene (Pressure Chemical Co. and Polymer Laboratories) and PMMA (Polymer Laboratories) standards were used in calibrating the system. The intrinsic viscosity-molecular weight relationships described in Ref. 21 were used to establish a universal calibration curve for the system. When the three-column arrangement was used, distinct elution times were seen for dimer, trimer, tetramer, pentamer, and hexamer as was observed earlier.¹³ The UV absorption below 254 nm resulting from the terminal unsaturation of these PMMA macromers was also observed.¹³

RESULTS AND DISCUSSION

The results of the gravimetric analysis of the reactor effluent are plotted as a function of time in Figure

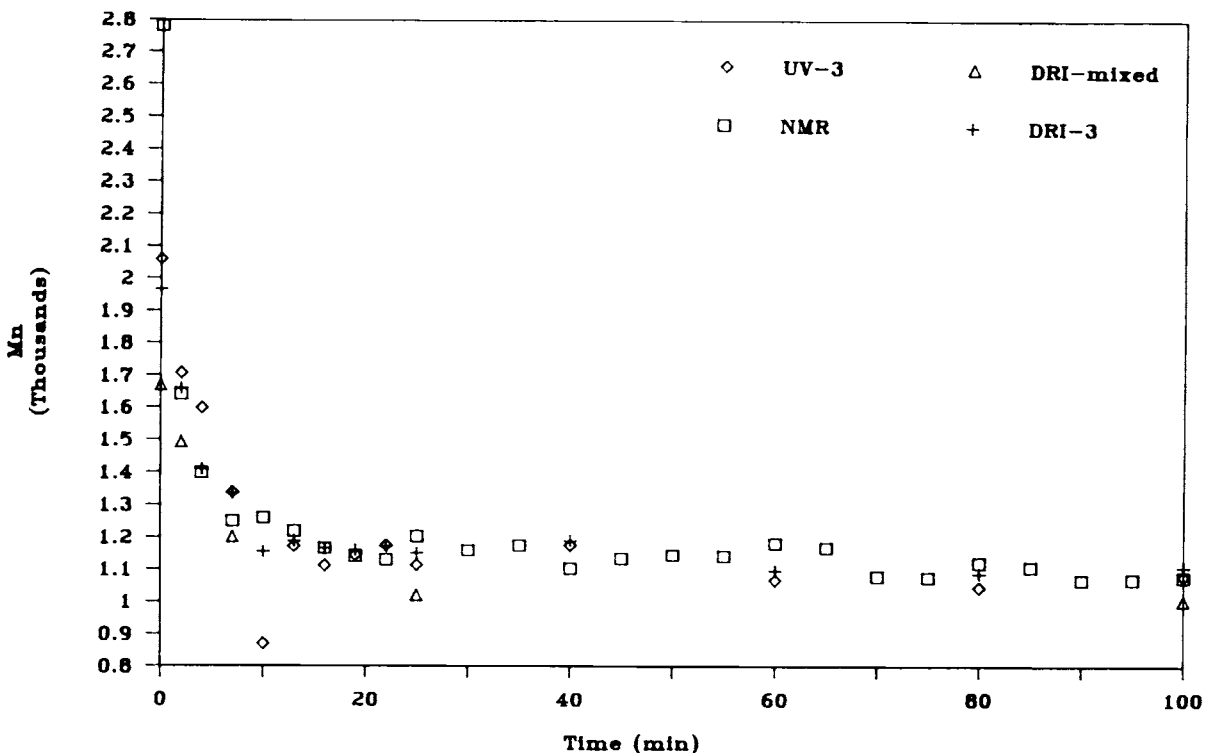


Figure 6 Number average molecular weight vs. time plot for PMMA macromer tubular reactor run at 12.5 ppm COBF as measured using four different methods.

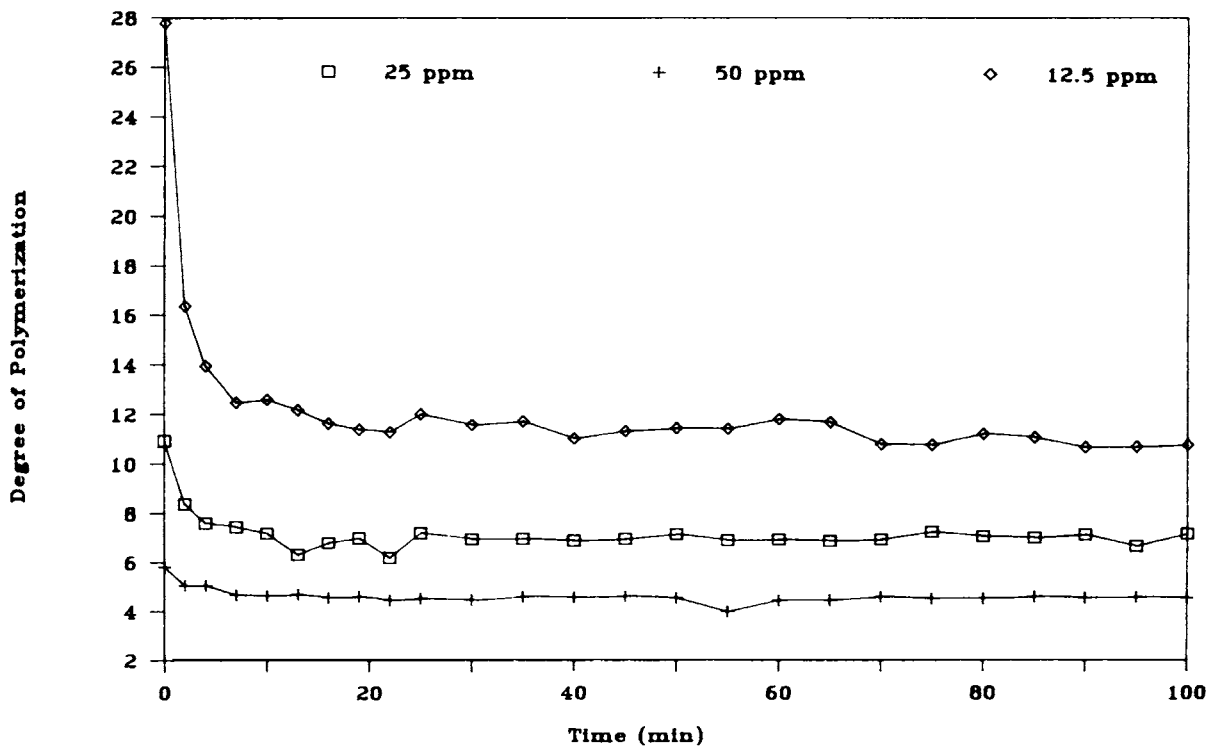


Figure 7 Number average degree of polymerization vs. time plot for PMMA macromer tubular reactor runs as determined by ¹H-NMR.

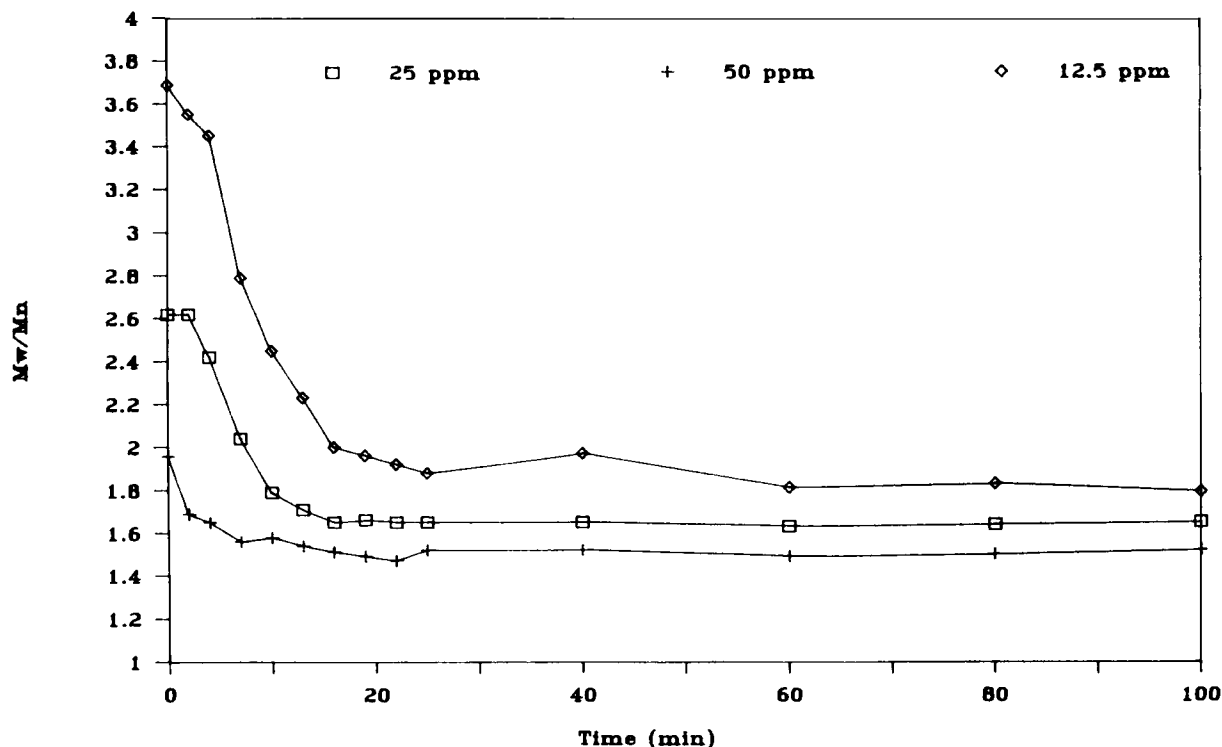


Figure 8 Polydispersity vs. time plot for PMMA macromer tubular reactor runs as determined by DRI using the three-column GPC arrangement.

5. All three runs behave in a similar manner; the conversion is initially low but increases over two mean residence times until a steady-state conversion is reached. This transient is believed to result from inhibition caused by oxygen initially present in the reactor. The magnitude of this oxygen-induced inhibition diminishes until the steady-state conversion is reached. This results from the oxygen being removed from the system as the reaction proceeds.

There is no apparent trend in conversion with respect to COBF concentration. The steady-state conversions (from 22 min on) are approximately 14%. This compares favorably with that predicted assuming plug flow and using classical free radical polymerization kinetics (predicted conversion 14.9% at 86°C, k_p and k_t from Ref. 22, k_d from Ref. 23, and 0.6 assumed for f). It has been shown earlier¹³ that the polymerization of MMA in the presence of COBF obeys classical kinetics, and it appears that plug flow behavior adequately describes the conversion in these tubular reactor runs. This is consistent with the observations of Cunningham¹⁷ with higher molecular weight polymers in a tubular reactor.

For each sample, the macromer number average molecular weights are presented in Table II. The columns headed NMR, 3 DRI, 3 UV, and M DRI

represent the molecular weights as determined by proton NMR, GPC using the 3 PL-gel columns and DRI detector, GPC using the 3 PL-gel columns and UV detector, and GPC using the mixed-bed column and DRI detector, respectively. These values are plotted for the 12.5 ppm COBF run in Figure 6, where the good agreement between these various methods is apparent. The NMR number average molecular weight-time data for the three runs are plotted in Figure 7 in order to facilitate comparisons between the runs.

Figure 7 indicates a similar behavior for all three runs. The macromer initially emerging from the reactor is of relatively high molecular weight, but the product molecular weight decreases to a steady-state value over the first two residence times. The difference between the initial and steady-state molecular weights lessens as the concentration of COBF in the system is increased. The cause of this transient is closely related to the cause of the conversion transient. It is believed that the oxygen initially present in the reactor oxidizes the COBF, destroying its catalytic activity. The expected effect of this on molecular weight would be greater as the concentration of COBF is lowered, since a larger proportion of the COBF would become oxidized. The poisoning of this

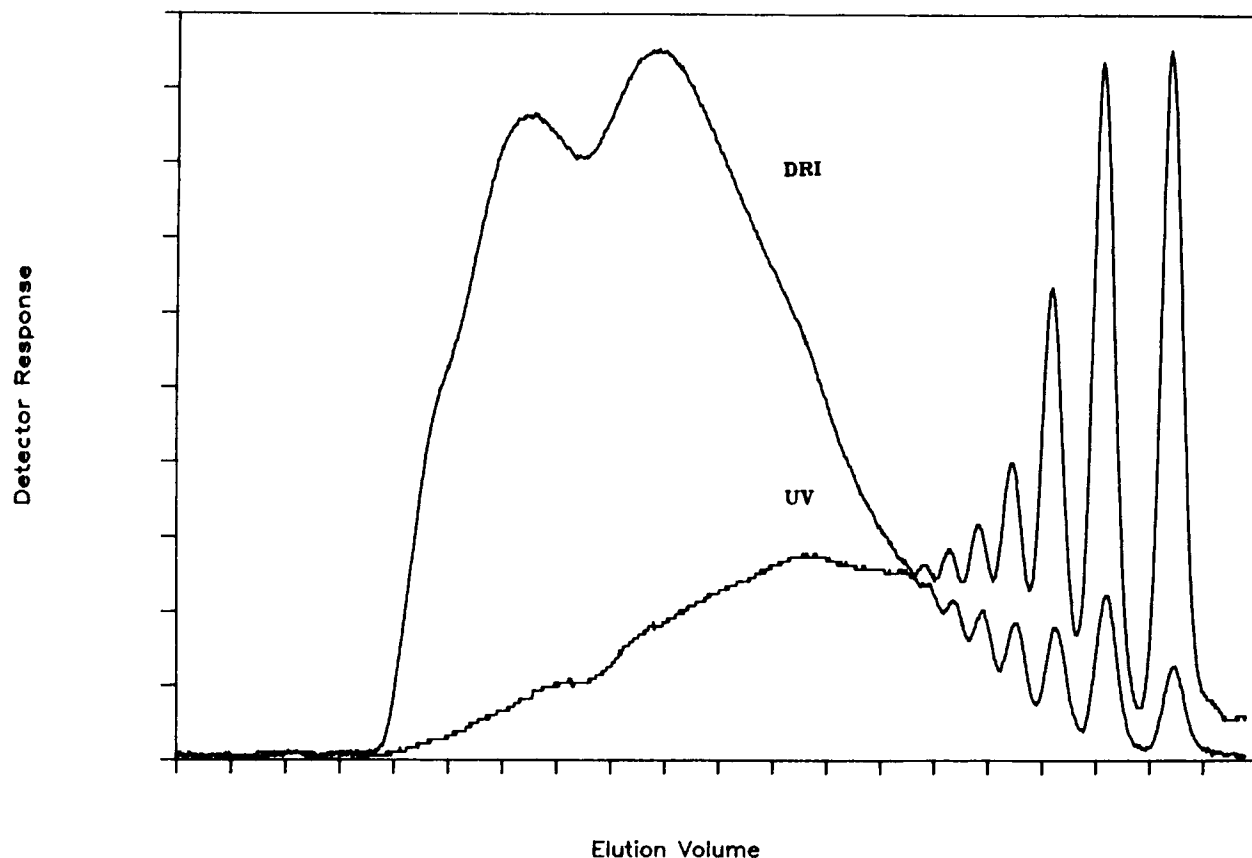


Figure 9 DRI and UV traces for the initial product from the 12.5 ppm COBF tubular reactor run.

CCTA by oxygen is not unexpected since cobaloximes have previously been found to be very sensitive to oxygen deactivation.¹²

Higher moments of the molecular weights could be determined using the GPC data and were used to determine the polydispersity (M_w/M_n) of the samples. These values are plotted against time in Figure 8. In light of the trends observed with time for conversion and number average molecular weight, it is not surprising that, for each run, the polydispersity begins high but reaches a lower steady-state polydispersity within two mean residence times. Also, the difference between the initial and the steady-state polydispersity increases as the COBF concentration goes down. These observations can also be attributed to poisoning of the COBF by oxygen initially present in the reactor.

It was noted from the GPC traces in the early samples that the macromers possessed a bimodal molecular weight distribution (see Fig. 9, UV and DRI GPC traces for initial product from 12.5 ppm run). As the run proceeded, the contribution from the high molecular weight peak diminished until it

is no longer evident. The bimodal nature of the macromers produced in the transient suggests that there is mixing in the reactor since it is unlikely that two products with distinct molecular weights will be formed in the reactor once it is filled. Hence, some of the high molecular weight product, formed when the reactor is being filled, must have been mixed with the macromers formed later in the reactor.

It is interesting to note that the steady-state polydispersities of all three runs are below the theoretical lower limit of two for polymer chains terminated by chain transfer. The highest experimentally determined steady-state polydispersity is 1.87 and the steady-state polydispersity decreased with increasing COBF concentration. This phenomenon has been observed earlier and is a characteristic of the molecular weight distributions of low molecular weight macromers synthesized using catalytic chain transfer agents.¹³

The efficiency of the COBF used in this study was compared with that used in ampule work¹³ using the chain transfer coefficient, C_s , as a measure of efficiency. The values calculated for C_s in this work

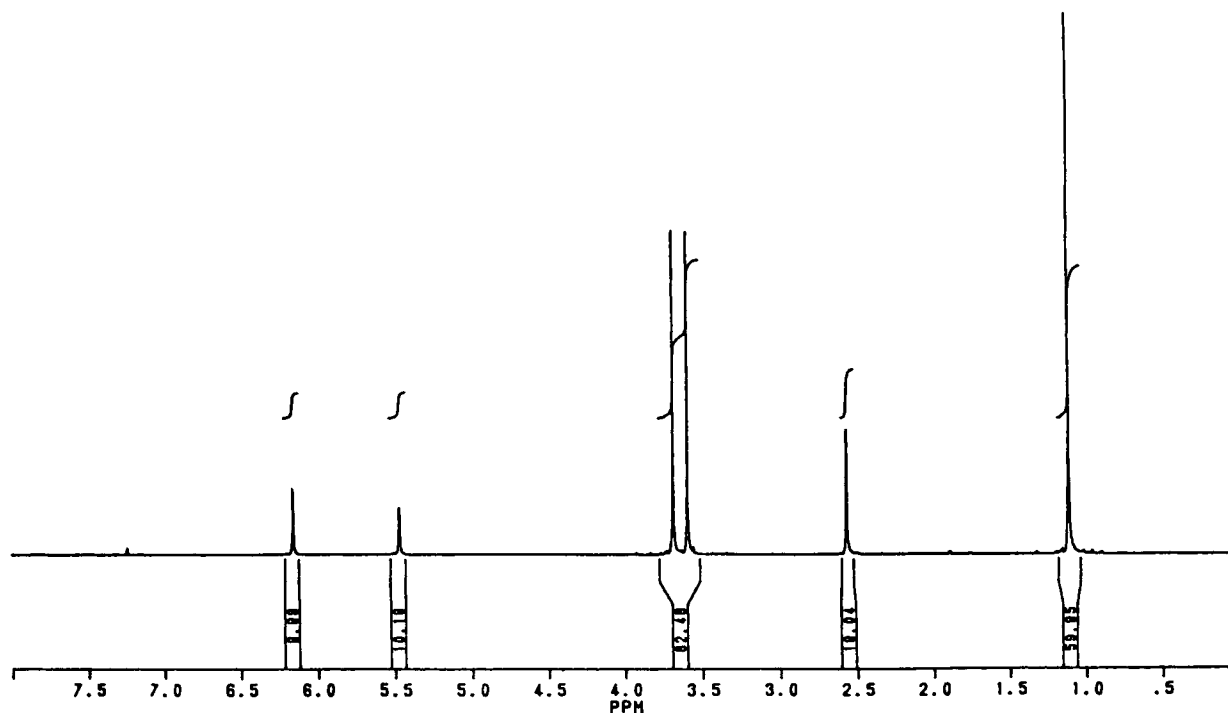


Figure 10 $^1\text{H-NMR}$ spectrum of PMMA macromer dimer fraction.

were 1.791×10^4 , 2.334×10^4 , and 2.875×10^4 for the runs at 50, 25, and 12.5 ppm, respectively. The value obtained for C_s from the literature Arrhenius expression¹³ at 86°C is 3.105×10^4 . It would not be correct to compare the constants determined for the runs at 25 and 50 ppm with this value since C_s for COBF was found to exhibit a chain-length dependence at low molecular weights¹³ and the Arrhenius expression is only valid for the limiting C_s . The run at 12.5 ppm may be used for comparison, however, and it is within the error of this expression. This value of C_s corresponds to a temperature of 94°C in the Arrhenius expression and may be a reflection of the slightly nonisothermal behavior of the tubular reactor.

The efficiency of the monomer removal from the polymerization reactor effluent by the twin-screw extruder was investigated. Here, the efficiency of monomer removal is expressed as the percentage of monomer in the extruder feed removed by the devolatilization process. The efficiency of monomer removal was 96.4, 98.2, and > 99.9% for the 50, 25, and 12.5 ppm COBF, respectively. It should be noted here that in the 12.5 ppm run that the vacuum gauge was malfunctioning. Full vacuum was inadvertently pulled in this case. Although this led to better devolatilization, it also resulted in poor monomer recovery. The low efficiency in the 50 ppm case can

be attributed to having two cool zones (zone 6 at 20°C and zone 7 at -10°C) before the die. These cool zones were required to obtain a suitable extrusion viscosity. These low temperatures serve to limit the driving force for devolatilization in these zones, however, and effectively shorten the diffusion-controlled devolatilization region. In general, however, it can be seen that this extruder configuration allowed the efficient devolatilization of a material that underwent a large viscosity and composition change during the devolatilization process.

The number average molecular weights of the macromer in the extrudates were measured using NMR. These were 1334, 752, and 480 for the 12.5, 25, and 50 ppm COBF runs, respectively. These numbers are higher than those obtained for the steady states in these polymerizations. The increased molecular weights of the extrudate likely result from both the feeding of small amounts of bimodal polymer (formed during the transient portion of the polymerization) to the extruder and from the removal of low molecular weight macromers from the extruder during the devolatilization. It was found that the dimer ($^1\text{H-NMR}$ spectrum given in Fig. 10) could be distilled from the 50 ppm polymerization reactor product at 72°C and 73 Torr. This boiling point differs from those reported in the literature, 110°C at 0.2 Torr (Ref. 1), 136–138°C at

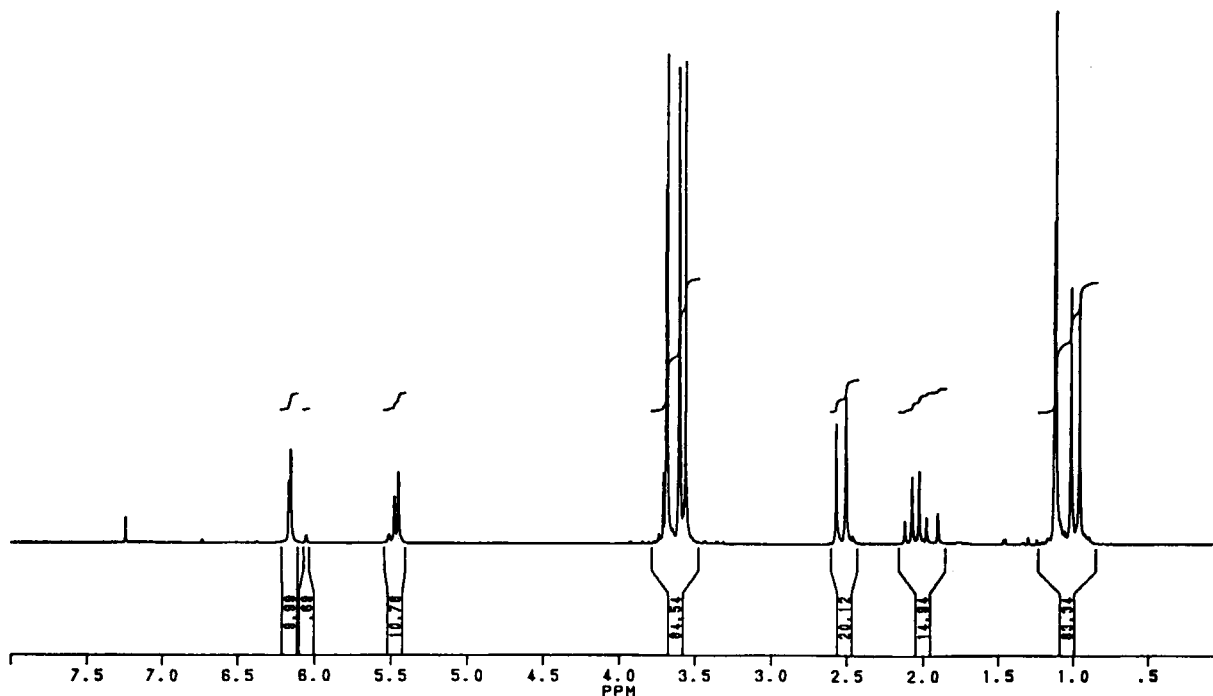


Figure 11 $^1\text{H-NMR}$ spectrum of PMMA macromer trimer-rich fraction.

50 Torr (Ref. 24), and 50°C at 0.9 Torr (Ref. 25). The same experiment was repeated and the same boiling point obtained. The distillate was examined by the three-column GPC arrangement and was found to be monodisperse ($M_w/M_n < 1.01$) with number average molecular weights of 202 and 200 as determined by DRI and UV, respectively. A second fraction was obtained at 122°C at 73 Torr. This was analyzed by $^1\text{H-NMR}$ (Fig. 11) and found to be rich in trimer. Reference 1 reports a boiling point for the trimer of 150°C at 0.2 Torr. It is evident that a fraction of the low molecular weight macromers is being removed during devolatilization. This may explain, in part, the increase in molecular weight found in the extruder devolatilized macromer.

In summary, a continuous process for the synthesis and isolation of macromers was developed. Significant features of this synthesis are that stable steady-state operation is obtained in less than two residence times and that during this steady-state operation the products are comparable to those formed in ampule work performed under analogous conditions. Hence, it is possible to make kilogram quantities of these macromers yet maintain the same degree of control over the final product as is realized in ampule polymerizations. Future work with these macromers will involve the preparation of graft copolymers.

The authors would like to express their appreciation to M. Cunningham, M. Mlekuz, and J. Pronovost for their assistance in this research. Support of this research by the Ontario Center for Materials Research (OCMR) and the National Science and Research Council of Canada (NSERC) is gratefully acknowledged.

REFERENCES

1. P. Cacioli, D. G. Hawthorne, R. L. Laslett, E. Rizzardo, and D. H. Solomon, *J. Macromol. Sci. Chem.*, **A23**(7), 839 (1986).
2. Y. Kawakami, *Encyclopedia of Polymer Science and Engineering*, Vol. 9, Wiley, New York, 1987, p. 195.
3. K. Kanzanskii, P. Kubisa, and S. Penczek, *Russ. Chem. Rev.*, **56**(8), 777 (1987).
4. P. Rempp and E. Franta, *Adv. Polym. Sci.*, **58**, 1 (1984).
5. R. Asami and M. Takaki, *Makromol. Chem. [Suppl.]*, **12**, 163 (1985).
6. T. Corner, *Adv. Polym. Sci.*, **62**, 95 (1984).
7. G. F. Meijs and E. Rizzardo, *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.*, **C30**, 305 (1990).
8. Y. Gnanou and P. Lutz, *Makromol. Chem.*, **190**, 577 (1989).
9. Y. Tsukahara, K. Mizuno, A. Segawa, and Y. Yamashita, *Macromolecules*, **22**, 1546 (1989).
10. G. Schulz and R. Milkovich, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 1633 (1984).

11. N. S. Enikolopyan, B. R. Smirnov, G. V. Ponomarev, and I. M. Belgovskii, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 879 (1981).
12. A. F. Burczyk, K. F. O'Driscoll, and G. L. Rempel, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3255 (1984).
13. R. Amin Sanayei and K. F. O'Driscoll, *J. Macromol. Sci. Chem.*, **A26**(8), 1137 (1989).
14. R. Amin Sanayei, Ph.D. Thesis, University of Waterloo, 1989.
15. A. Rudin, *The Elements of Polymer Science and Engineering*, Academic Press, New York, 1982, p. 364.
16. B. Tarmy, *Encyclopedia of Polymer Science and Engineering*, Vol. 14, Wiley, New York, 1988, p. 224.
17. M. Cunningham, Doctoral Thesis, University of Waterloo, 1990.
18. J. Biesenberger, *Chem. Eng. Prog.*, **June**, 55 (1987).
19. S. Lee and J. Biesenberger, *Polym. Eng. Sci.*, **29**(12), 782 (1989).
20. M. Cunningham, K. F. O'Driscoll, and H. K. Mahabadi, *Can. J. Chem. Eng.*, to appear.
21. C. Tsitsilianis, G. Mitsiani, and A. Dondos, *J. Polym. Sci. B Polym. Phys.*, **27**, 763 (1989).
22. H. K. Mahabadi and K. F. O'Driscoll, *J. Macromol. Sci. Chem.*, **A11**(5), 967 (1977).
23. Du Pont VAZO™ 52 Technical Literature.
24. S. McElvain and C. Aldridge, *J. Am. Chem. Soc.*, **75**, 3987 (1953).
25. T. Kealy and R. Benson, *J. Org. Chem.*, **26**, 3126 (1961).

Received September 25, 1990

Accepted January 2, 1991