Polymer Bulletin 21, 439–444 (1989)

Polymer Bulletin

The effect of continuous slow monomer addition technique on cationic polymerization in liquid sulfur dioxide

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Summary

The polymerizations of styrene and alpha-methylstyrene in liquid sulfur dioxide have been investigated by the use of the slow, continuous monomer addition technique in the presence of m-chloroperbenzoic acid or CF_3SO_3H as initiator. Quasiliving polymerization has been obtained in Sty/MCPBA/-40°C/liquid SO_2 system. The formed polymer is insoluble in the medium indicating that in liquid SO_2 the propagating species remain active even in a heterogeneous system.

Introduction

In some carbocationic polymerization systems chain transfer and termination are absent or reversible. This way, it is possible to avoid these side reactions by employing special conditions. One of the most important techniques used to depress chain transfer to monomer, The quasiliving technique, has been developed by J.P.Kennedy et al. and is based on a continuous slow monomer addition to the initiating system.(1,2) For the success of these reactions it is necessary to carry them out in an homogeneous medium with good stirring and on a continuous slow monomer flow in order to maintain a suitable low monomer concentration in the charge.(2)

In the course of our continued investigations using liquid sulfur dioxide as the solvent in cationic polymerizations initiated by m-chloroperbenzoic acid we noted that: a) the molecular weight increases linearly with the monomer/initiator ratio (3); b) chain transfer to monomer is diminished by using styrene as the monomer (4); c) in alpha-methylstyrene - styrene copolymerizations, the former monomer is more reactive (5) and this difference in reactivity favors the formation of block segments in the copolymer. (6)

As the high ionizing power of this solvent and its ability in solvate the counteranion prevent termination reactions, we became interested to know how the continuous monomer addition technique influences our polymerization system. This paper concerns our preliminary results using m-chloroperbenzoic acid (MCPBA) or trifluormethanesulfonic acid (CF_3SO_3H) as the initiator.

Experimental

Materials

Styrene(Sty), alpha-methylstyrene (AMS), dichloromethane and MCPBA were purified according to the procedure previously described.(6,7) CF_3SO_3H was distilled under vacuum and stored in sealed ampules.

Procedures

Polymerizations were performed under N_2 in an apparatus previously described.(8) In a dry 100 ml. three-necked flask were placed the SO_2 liquefied by a Dewar condenser and the initiator dissolved in 2 ml. of dichloromethane. The mixture was maintained at -20°C during 5 min. to form the m-chlorobenzoylsulfuric acid, the actual initiator in this system.(7) Then, the reaction temperature was kept at -40°C or -60°C and the monomer was continuously slowly added. The increase of molecular weight with monomer input was followed by withdrawing aliquots from time to time and injecting them into excess methanol.

Molecular weights were obtained by a Toyo-Soda GPC equipped with two columns (10^3,10^6 A) and dual UV and RI detectors. A universal calibration curve using polystyrene standards was used.

Results and Discussion

In Table 1 are listed the results concerning the polymerization initiated by MCPBA using the continuous slow monomer addition technique. In Fig. 1, the plot of polymerization degree versus monomer input shows that $\overline{DP}_n$ increases linearly at the first stage of the Sty polymerization at -40°C (Exp. nº BQ-23). As it was reported by J.P.Kennedy (1) this behavior and the fact that the total number of polymer molecules(P) (given by the $M_{total}/\overline{DP}_n$ ratio), remain practically unchanged at this stage, suggest quasiliving conditions and the absence of chain transfer. It should be emphasized that this experiment was carried out in liquid sulfur dioxide, in which polystyrene is insoluble. These results are not in agreement to the theory proposed by J.P.Kennedy that the quasiliving conditions are not satisfied in highly viscous polymer solutions where stirring is difficult.(2) We suggest that the Sty/MCPBA/liquid SO_2 is different in that the propagating species remain active even in a heterogeneous medium.

Table 1

Polymerization of Sty or AMS in MCPBA/liquid$_3$ SO$_2$ system, using the continuous slow addition technique; [MCPBA] : 5.96 x 10 M; SO$_2$: 28 ml.; CH$_2$Cl$_2$: 2 ml.

Exp. nº	monomer	temp. (°C)	rate of monomer addition (mol/l.min)	M_{total} (mol/l)	$\overline{M}_w$ x 10^{-3}	$\overline{M}_w/\overline{M}_n$	$\overline{DP}_n$	(P) x 10^3
BQ-23	Sty	-40	0.19	0.40	94.0	2.7	334	1.19
				0.58	141.0	2.3	586	0.99
				0.78	180.0	2.1	788	0.99
				0.97	207.0	2.5	800	1.21
				1.45	204.0	2.0	980	1.48
BQ-28	Sty	-60	0.34	0.34	78.0	1.4	529	0.64
				0.69	170.0	2.7	596	1.15
				1.03	189.0	2.8	634	1.62
				1.45	202.0	3.0	644	2.25
BQ-19	AMS	-40	0.13	0.19	14.0	2.1	56	3.39
				0.25	12.0	1.7	59	4.24
				0.38	19.0	2.8	57	6.66
				0.54	15.0	2.3	55	9.80
BQ-17	AMS	-60	0.18	0.18	33.0	2.1	135	1.33
				0.49	23.0	2.6	76	6.44
				0.56	25.0	1.9	110	5.09

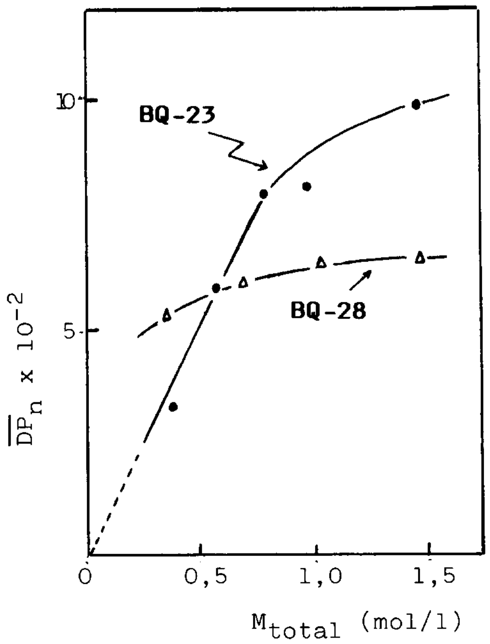

Fig. 1. $\overline{DP}_n$ vs monomer input plot of MCPBA/liquid SO_2 polym. system.

In Sty polymerization carried out at -60°C, we also noted an increase of molecular weight with the monomer input. In this case, however, the total number of macromolecules increases during the run, indicating some chain transfer to monomer. The deviation of linearity may be related to the higher monomer input rate, which increases the monomer concentration in the charge. As the total number of macromolecules (P) is less than the initiator concentration(Exp. nº BQ-23 and BQ-28 - Table 1), we can also suggest that even in a highly ionizing medium, the initiator efficiency is low.

In contrast, we cannot observe an increase of molecular weight with monomer input in the polymerizations of AMS under the conditions just described (Exp. nº BQ-19 and BQ-17). Probably due to the higher reactivity of AMS the monomer concentration in the charge is low enough so that irreversible chain transfer by indane formation can occur.

The continuous slow monomer addition technique was also employed in preliminary polymerizations in liquid SO_2 initiated by CF_3SO_3H. The results are shown in Table 2, where we can observe an increase of molecular weight with monomer input, in the case of Sty polymerization. The total number of polymer molecules (P) was always higher than the initiator concentration, indicating a higher initiator efficiency than with MCPBA and the presence of chain transfer to monomer. These results can be

Table 2

Polymerization of Sty or AMS in CF_3SO_3H/liquid SO_2 system, using the continuous slow addition technique; $[CF_3SO_3H]$: 2.5 x 10^{-3}M; SO_2: 28 ml.; CH_2Cl_2: 2 ml.

Exp.nº	monomer	temp. (°C)	rate of monomer addition (mol/l.min)	M_{total} (mol/l)	$\overline{M}_w$ x 10^{-3}	$\overline{M}_w/\overline{M}_n$	$\overline{DP}_n$	(P) x 10^3
BQ-30	Sty	-40	0.24	0.49	30.0	1.8	157	3.10
				0.74	54.0	1.8	288	2.56
				1.23	81.0	2.3	331	3.71
				1.45	83.0	2.3	346	4.19
BQ-35	AMS	-40	0.17	0.34	11.0	1.3	67	5.07
				0.52	9.0	1.4	51	10.19
				0.69	9.0	1.6	42	16.43
				0.86	7.0	1.5	38	22.63
				1.03	6.5	1.5	34	30.29
				1.20	3.6	2.0	17	70.59

related to the lower nucleophilicity of the counteranion derived from CF_3SO_3H and the more dissociated propagating species which favors chain transfer.

In the case of AMS (BQ-35) the polymerization is completely dominated by chain transfer and the $\overline{DP}_n$ decreases with monomer input.

Acknowledgments

Financial support by Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro(FAPERJ) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) is gratefully acknowledged. Authors are also grateful to the Instituto de Macromoléculas - UFRJ, for the GPC analysis.

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Accepted April 4, 1989 K