Polymer Bulletin 33, 405–409 (1994)

Polymer Bulletin

Cationic polymerization of α-methylstyrene in liquid sulfur dioxide initiated by *p*-methoxybenzyl chloride

Juan C. Rueda, Ailton S. Gomes*, and Bluma G. Soares

Instituto de Macromoléculas, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bl.J, 21945-970, Rio de Janeiro, Brazil

Summary

The cationic polymerization of α-methylstyrene (α-MeSty) in liquid sulfur dioxide initiated by benzyl chloride and p-methoxybenzyl chloride was investigated at different temperatures. The p-methoxybenzyl chloride (p-MOBCl) was found to be effective in initiating α-MeSty polymerization while benzyl chloride yielded only traces of polymer under all conditions. Polymers with narrow molecular weight distribution were obtained indicating rapid exchange between p-MOBCl dormant species and the corresponding carbenium ion. The reaction seems to be controlled by termination.

Introduction

The ability of aliphatic chlorides in conjunction with different Lewis acids as initiating systems for cationic polymerization is well established in literature (1). Important syntheses have been achieved by appropriate combination of both components, that is, the cationogen (aliphatic chloride) and the activator (Lewis acid). One interesting research in this field has been developed by Kennedy and co-workers including a series of papers concerning the use of INIFER - based systems on synthesis of telechelic polyisobutylene (1-4). Other authors have also employed similar initiating systems in polymerization of other monomers (5-6).

Recently it was stated that a living cationic polymerization could be achieved by using a particular alkyl chloride / Lewis acid system together with the addition of salts with common anion and in solvents of low polarity (7-9). An equilibrium between active carbenium ions and inactive dormant species is suggested whose position depends on the leaving group in the initiator, the Lewis acid strength, reaction medium and monomer structure (7-10). A narrow molecular weight distribution can be obtained with weaker Lewis acid, among other factors (10).

All polymerizations just discussed were performed in conventional solvents like toluene, dichloromethane, 1,2-dichloro-ethane, and so on. A peculiar behavior is observed in cationic polymerizations in the presence of liquid sulfur dioxide. Because of its high ionizing power and its ability in solvating the counteranion, liquid SO_2 provides fast reactions with initiators like percompounds (11), Lewis acids (12) and iodine (13-15). The polymerization of α-MeSty in iodine / SO_2 system was carried out with a minimum of chain transfer or termination as a result of the nucleophilic nature of this counteranion and the ionizing characteristic of the solvent. The role of SO_2 as Lewis acid was also evidenced in some reports concerning the polymerization initiated by alkyl (16) or acyl halides (17).

---

*Corresponding author

In view of these observations, particularly the influence of the Lewis acid strength in obtaining polymers with narrow MWD we decided to investigate the behavior of α-MeSty polymerizations initiated by organic halides in liquid SO_2. In this communication, we report our results concerning the polymerization initiated by benzyl chloride and p-MOBCl.

Experimental

materials. α-MeSty, sulfur dioxide and dichloromethane were purified as described (13). Benzyl chloride was destilled twice under reduced pressure and kept under dry nitrogen at -10°C. p-Methoxybenzyl chloride (p-MOBCl) was prepared by reduction of p-anisaldehyde followed by chlorination of the p-methoxybenzyl alcohol (18).

procedure. All polymerizations were carried out under dry nitrogen in a glass equipment previously described (11,13-15). The reactors, cooled to the desired temperature, were charged with the solvent (liquid SO_2) and the monomer. Reactions were started by adding a precooled solution of an alkyl chloride in dichloromethane, and quenched by adding 1 ml of prechilled methanol. The molecular weights of the polymeric materials were determined with a Toyo-Soda high-speed liquid chromatograph HLC-803A equipped with a RI detector and three ultrastyragel columns (2 linear and 500 Å) using toluene as a solvent. The values of Mn and Mw/Mn were obtained using polystyrene calibration.

Results and Discussion.

α-MeSty was polymerized in p-MOBCl / SO_2 system at different temperatures. The results concerning the effect of initiator concentration and temperature are presented in Table 1. In almost all conventional cationic polymerization systems, an increase of molecular weight with decreasing temperature is observed as a result of decreasing side reactions like chain transfer. In contrast, according to the data just presented, the molecular weights seem to be independent on temperature. Considering the same initiator concentration, a decrease in temperature affects mainly the conversion and consequently the average number of polymer chains, **P**. At lower temperatures, the **P** values are smaller than the initiator concentration indicating decreasing of chain transfer and initiator efficiency. Decreasing [p-MOBCl] also decreases the conversion. For reactions performed at -20°C, the initiator efficiency increases with decreasing the [p-MOBCl].

No great differences were observed in conversions for polymerizations performed at -40°C and -60°C with the same [p-MOBCl]. Nevertheless, the molecular weights obtained at -60°C were slightly lower. Considering the very narrow MWD of polymers obtained at this temperature, the decrease of molecular weights may indicate an increase of initiator efficiency.

According to the concept of equilibration between active carbenium ions and inactive dormant species proposed by several authors (7-10), an equilibrium between non-dissociated p-MOBCl and its active carbenium ion may be taking place in this system. It seems that a rapid exchange between these species is happening considering the narrow molecular weight distribution obtained even at -20°C. The values achieved in this system are similar or narrower than those reported by Matyjaszewski and co-workers for the living cationic polymerization of α-MeSty by cumyl chloride/ $SnCl_4$ system in the presence of a common anion salt (10).

Higher p-MOBCl concentration corresponds to higher carbenium ion concentration which causes an increasing in the number of propagating chains and in the overall rate of propagation. For each temperature, the conversion increases with the initiator concentration although these values are small.

Table 1

Polymerization of α-MeSty with p-MOBCl/ SO_2 [a]

temperature (°C)	[p-MOBCl] mM	conversion [b] (%)	Mn	MWD	P [c] mM	I_{eff} (%)
-20	36.8	43	920	1.16	44.3	120.4
-20	26.9	35	1120	1.36	29.8	110.8
-20	23.0	45	1350	2.33	31.7	137.8
-20	18.4	33	1230	1.45	25.7	139.6
-20	9.0	28	1160	1.53	23.0	255.0
-40	36.8	22	1350	1.15	15.4	41.8
-40	26.9	16	1930	1.31	8.0	29.7
-40	23.0	15	2080	1.26	6.8	29.6
-40	18.4	12	2100	1.29	5.5	29.9
-40	9.0	8	2150	1.27	3.5	38.8
-60	36.8	23	1260	1.03	17.3	47.0
-60	26.9	15	1470	1.03	9.7	35.7
-60	23.0	13	1610	1.02	8.0	34.8
-60	18.4	10	1490	1.04	6.4	34.5
-60	9	7	1760	1.02	3.9	42.8

a) [α-MeSty] = 0.809 M; SO_2 = 8 mL; reaction time = 120 min.
b) conversion determined from insoluble material in methanol.
c) average number of polymer chain calculated by $[([M]_0 - [M]) / DPn]$

The effect of time on conversions and molecular weights was also investigated and the results are shown in Table 2. The variation of conversion with time is better illustrated in Figure 1 which shows increasing conversion in the beginning of the reaction without induction period. After ~ 1 hour, the reaction seems to stop. These features are observed at all temperatures and suggest a rapid exchange between active and dormant initiator species but slow propagation which favors termination.

Attempts have been made to polymerize α-MeSty using the benzyl chloride / SO_2 system but this halide remained practically inactive in SO_2 .

Table 2

Effect of Time on α-MeSty Polymerization with p-MOBCl/ SO_2 [a]

temp (°C)	time (min)	conversion (%)	Mn	MWD	P^b (mM)	I_{eff} (%)
-20	30	20	1140	1.30	16.7	72.6
-20	60	35	1270	1.67	26.7	116.1
-20	120	45	1350	2.33	31.7	137.8
-20	180	46	1340	2.12	33.0	143.5
-40	30	6	1270	1.24	4.8	20.8
-40	60	12	2070	1.22	5.6	24.3
-40	120	15	2080	1.26	6.8	29.6
-40	180	18	1970	1.30	8.9	38.7
-60	30	5	1210	1.02	4.3	18.7
-60	60	11	1240	1.03	8.5	36.9
-60	120	13	1610	1.02	8.0	34.8
-60	180	14	1390	1.04	9.8	42.6

a) [α-MeSty] = 0.809M; [p-MOBCl] = 23mM; SO_2 = 8 mL.
b) P as in Table 1.

Conclusions

p-MOBCl is able to initiate the polymerization of α-MeSty in liquid SO_2. In spite of the high dielectric constant of the medium, polymers with narrow MWD were obtained without the addition of common anion salt. These narrow MWDs are attributed to the rapid exchange between carbenium ions and p-MOBCl dormant species. The position of this equilibrium is controlled by the leaving group, by Lewis acid strength, by the medium, and determines the overall rate of propagation. In our system, the equilibrium is easily reached but its position is displaced to the dormant species because of the weak SO_2 as Lewis acid and because of the poor chloride leaving group. SO_2 can ionize p-MOBCl because of the relatively high stability of the corresponding carbenium ion but is not effective with benzyl chloride.

Additional experiments with other aliphatic chlorides, including cumyl chloride, are being performed to achieve a balance among Lewis acid, leaving group, monomer and polarity of the medium. The results will be published later.

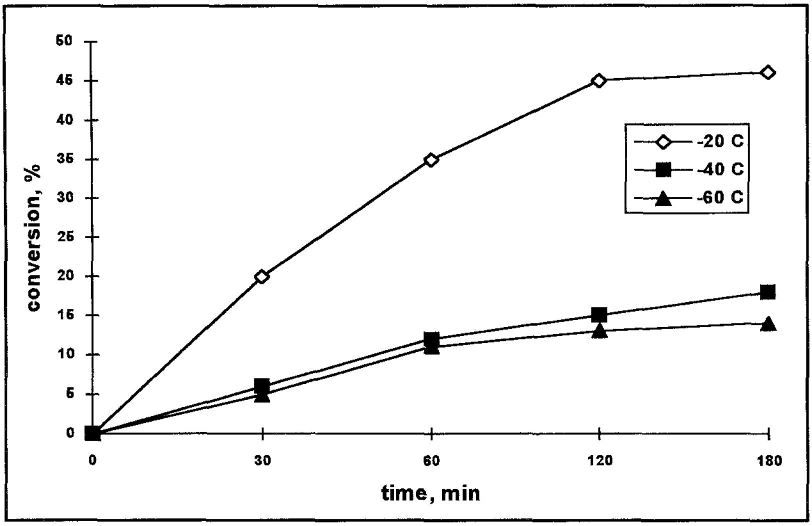

Figure 1. Variation of conversion with the time for α-MeSty polymerization with p-MOBCl/SO_2; [α-MeSty] = 0.809 M; [p-MBCl] = 23mM; SO_2 = 8 mL.

Acknowledgments

The authors are indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Conselho de Ensino para Graduados e Pesquisa (CEPG-UFRJ), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and PADCT-FINEP for financial support.

References.

1. Kennedy, J.P., Maréchal, E., Carbocationic Polymerization, John Wiley & Sons, New York, 1982.
2. Bisma, M., Kennedy, J.P., Makromol. Chem., Macromol. Symp., 1986, 3, 113
3. Kennedy, J.P., Smith, R.A., J. Polym. Sci., Chem. Ed., 1980, 18, 1523
4. Kennedy, J.P., Huang, S.Y., Feinberg, S.C., J. Polym. Sci., Chem. Ed., 1977, 15, 2869
5. Nuyken, O., Pask, S.D., Vischer, A., Walter, M., Makromol. Chem., 1985,186, 173
6. Pokonny, T.S., Spevácek, J., J. Polym. Sci., Chem. Ed., 1989, 27, 2217
7. Ishihama, Y., Sawamoto, M., Higashimura, T., Polymer Bull., 1990, 24, 201
8. Kennedy, J.P., Ivan, B., Designed Polymer by Carbocationic Macromolecular Engineering, Theory and Practice, Hanser, Oxford, 1992.
9. Sawamoto, M., Progress in Polym. Sci., 1991, 16, 111
10. Matyjaszewski, K., Bon, A., Lin, C.H., Xiang, J.S., Polym. Prep., 1993, 34 (1), 487
11. Soares, B.G., Gomes, A.S., J. Polym. Sci., Chem. Ed., 1987, 25, 1105
12. Tokura, N., Matsuda, M., Ogawa, Y., J. Polym. Sci.,1963, Part A-1, 1, 2965 and references therein.
13. Soares, B.G., Silva, A., Gomes, A.S., Polymer Bulletin, 1992, 29, 253 -258,
14. Silva, A., Gomes, A.S.,Soares, B.G., Polymer Bulletin, 1992, 29, 509 - 514,
15. Silva, A., Gomes, A.S., Soares, B.G., Polymer Bulletin, 1993, 30, 133 - 139,
16. Tokura, N., Kawahara, T., Bull. Chem. Soc. Japan, 1962, 35, 1902
17. Tokura, N., Kawahara, T., Watanabe, T., Bull. Chem. Soc. Japan, 1963, 36, 760
18. Vogel, A.I., A Textbook of Practical Organic Chemistry, 1956, Longman, 3nd ed.

Received: 10 May 1994/Revised version: 15 June 1994/
Accepted: 17 June 1994