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Synthesis of poly(methylmethacrylate) macromonomers prepared by radical chain transfer reaction H NMR study of macromonomer end-groups

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Summary

The end-group analysis for both PMMA telomers having a carboxyl end-group and macromonomers derived from these telomers was carried out using ^{1}H NMR. Telomers were prepared by telomerization of methyl methacrylate (MMA) with thioglycolic acid (TGA) initiated with 2,2' azobis(isobutyronitrile) (AIBN) in acetonitrile at 70°C. Then, macromonomers were obtained by reaction of the telomer carboxylic acid end-group with glycidyl methacrylate (GMA) using a chromium salt as catalyst. From the ^{1}H NMR study, it was found that the telomer/macromonomer conversion results from two ways of epoxy addition (α and β), as observed in a model reaction between GMA and octanoic acid (OA).

Introduction

Recent developments in polymer synthesis allow versatile molecular designs for supramolecular architecture (1). End-functionalized oligomers such as telechelics, and macromonomers have been utilized as one of the elementary structural units for the tailor-made construction of such architectures (2).

A macromonomer is an oligomer with an end-group that can copolymerize with comonomers to form comb type graft copolymers (3). In the last few years, the number of studies on the synthesis of macromonomers has rapidly increased (4).

Several methods have been described for making macromonomers including anionic polymerization (5,6,7), group transfer polymerization (8,9,10,11,12), addition fragmentation chain transfer (13,14), catalytic chain transfer to alkyl cobalt complexes (15,16,17) and free radical polymerization (18,19,20,21,22,23,24).

As a comparison, free radical chain polymerization is relatively easy to carry out, and it can be used to polymerize many monomers, including functional monomers, what is difficult or impossible with anionic, cationic, or group-transfer methods. Living polymerization (by ionic, coordination or group transfer mechanisms) is limited because of the restricted range of monomers that can be used and due to stringent requirements on reaction conditions and monomer purity. Catalytic chain transfer to alkyl cobalt complexes would be an interesting method, however, graft copolymer, which is the application of our macromonomer, has not been observed because fragmentation dominates over reaction with monomer (15).

In the field of macromonomer end-groups analysis, some works have been done. Mc Cord et al. (25) have examined end-groups and tacticity via ^{1}H and ^{13}C NMR of polymethyl methacrylate (PMMA) macromonomers and oligomers (n=1-4) made under conditions of cobalt catalyzed chain transfer.

In this work, as explained previously, radical chain transfer reaction has been chosen for macromonomer synthesis. This paper gives an account of the macromonomers synthesis of methyl methacrylate (MMA) by a two-step reaction. First one led to PMMA telomers having a carboxyl end-group which were in a second step converted to PMMA macromonomers by the reaction of carboxylic end-groups with glycidyl methacrylate (GMA).

Moreover, a detailed ^{1}H NMR study has been performed on the identification of the end-groups, and an attempt has been made to correlate observed spectra with both experimental and theoretical models.

Experimental part

(a) Synthesis

*□ **Telomers**:* Telomerization of methyl methacrylate (MMA) was performed at 70°C in acetonitrile using 2,2'-azobisisobutyronitrile (AIBN) as initiator in the presence of thioglycolic acid (TGA) as transfer agent. Telomerization was carried out with distilled monomer, under a nitrogen flow and vigourous stirring. Then telomers were obtained by precipitation into pentane.

*□ **Macromonomers:*** Telomers were converted to macromonomers by the reaction of the terminal carboxylic acid with glycidyl methacrylate (GMA) in toluene at 70°C for 12 hours in the presence of a small amount of hydroquinone and chromium salt as catalyst.

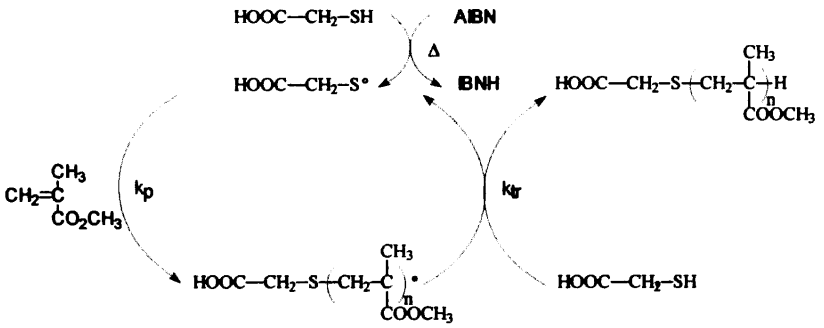
*□ **Catalyst synthesis:*** Chromium salt (chromium diisopropyl salicylate) was obtained from the reaction of chromic acetate and diisopropyl salicylate in refluxing methanol and subsequent removal of acetic acid formed under vacuum at 85°C.

(b) ^{1}H NMR

^{1}H NMR spectra were obtained with a BRUKER 200 MHz spectrometer using $CDCl_3$ solutions.

Results and discussion

In a previous work (26), we have studied the telomerization of MMA with thioglycolic acid (TGA) as transfer agent (Scheme 1)



Scheme 1 : Mechanism of telomerization

The kinetic study of this telomerization led to the determination of the TGA transfer constant (C_t = 0,67). Thus, by using this result and Mayo's law (27), the molecular weight of the telomer could be easily controlled.

$$\frac{1}{\left(\overline{DP_n}\right)_0} = C_T \frac{[T]_0}{[M]_0} \qquad \text{Mayo's law}$$

By this way, a low molecular weight telomer has been synthesized as described below ($\overline{DP_n}$ =15) (Figure 1). This molecular weight has been confirmed by G.P.C. ($\overline{M_n}$ =1600 $g.mol^{-1}$ / eq. PMMA).

$$\overline{DP_n} = \frac{p/3}{k/2}$$

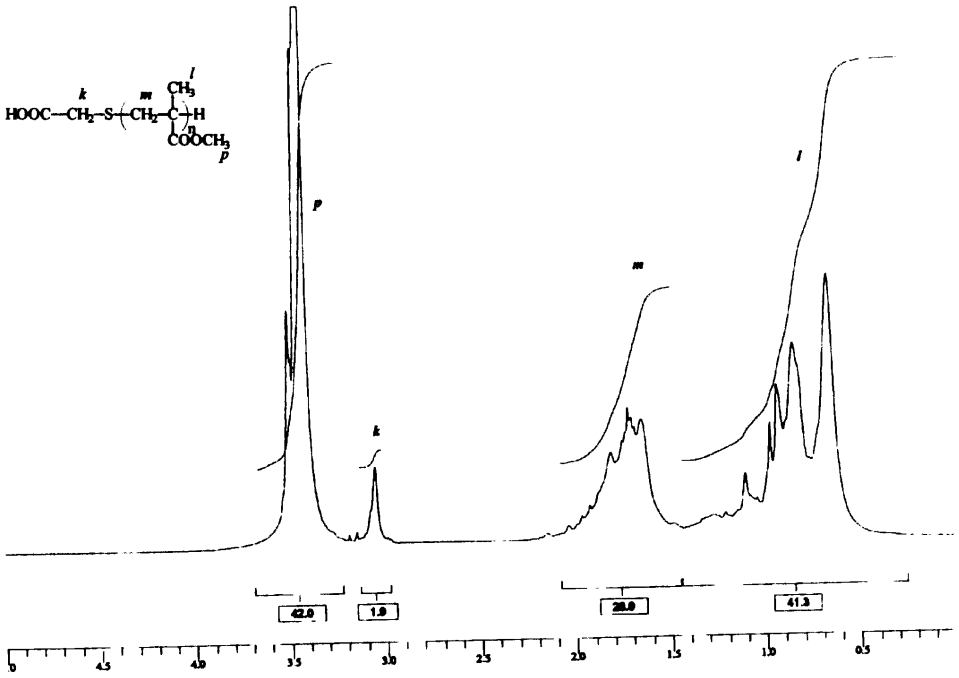
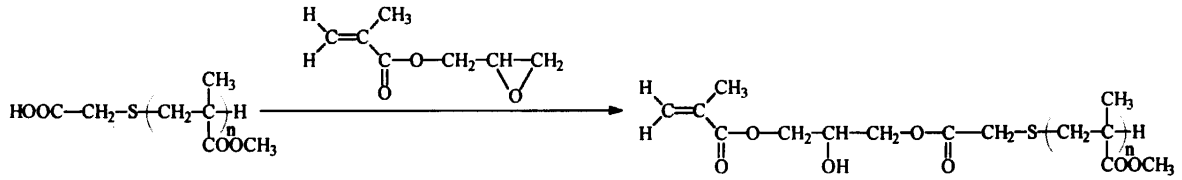


Figure 1: ^{1}H NMR of PMMA telomer ($\overline{DP_n}$ =15)

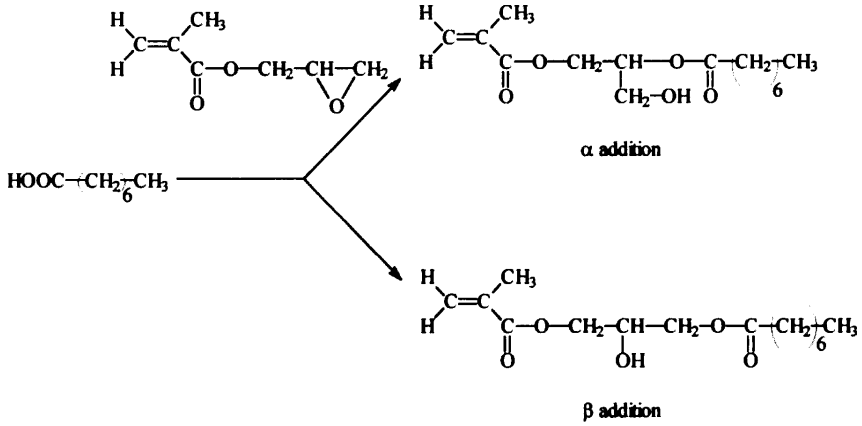
For the preparation of PMMA macromonomers, the following route (Scheme 2) was used :



Scheme 2 : Mechanism of macromonomers synthesis

Ohtani et al. (28) and Tsukahara et al. (29) used this method with N,N dimethyllaurylamine as catalyst in xylene at 140°C. Our aim has been to reduce the temperature of the reaction (70°C) by using an other epoxy-carboxy catalyst which is a chromium salt as described by Uri (28).

Prior to the synthesis and the ^{1}H NMR study of the macromonomer we have found interesting to investigate the carboxy-epoxy reaction between GMA and octanoic acid (OA) as model. This reaction is the result of two ways of addition (Scheme 3).



Scheme 3 : Carboxy-epoxy model reaction

The ^{1}H NMR study confirms this model (Figure 2).

The assignment of signals on Figure 2 confirmed that the products obtained were formed via α (80%) and β (20%) additions. These results were obtained by comparison of protons integrations as follows:

$$\alpha = 1 - \beta$$

$$\beta = \frac{e'}{a + a'}$$

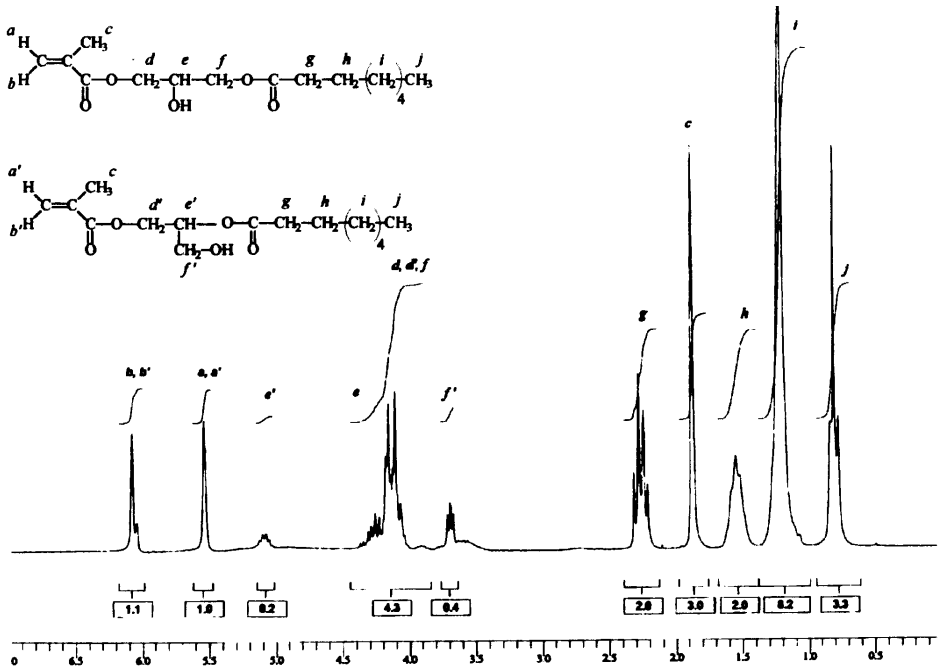


Figure 2 : ^{1}H NMR of products resulting of carboxy-epoxy model reaction

In order to confirm the assignments on Figure 2 we have simulated the same reaction with ^{1}H NMR ACD software. This simulation listed in Table 1 is in good agreement with the experimental values.

	a a'	b b'	c	d d'	e	e'	f	f'	g	h	i	j
^{1}H NMR theoretical (ACD)	5,60	6,10	1,88	3,98 to 4,17	4,41	5,13	3,93 to 4,10	3,72 to 3,79	2,29	1,49	1,28	0,88
^{1}H NMR experimental	5,5	6,1	1,9	4,1	4,3	5,1	4,1	3,7	2,3	1,5	1,3	0,8

Table 1 : Comparison of theoretical and experimental ^{1}H NMR shifts for carboxy-epoxy model reaction

Operating as previously, the reaction between GMA and carboxylic end-groups of PMMA telomers was performed (yield of reaction ≈ 95%). Referring to PMMA telomer and carboxy-epoxy ^{1}H NMR study, the assignment was carried out and is given in Figure 3.

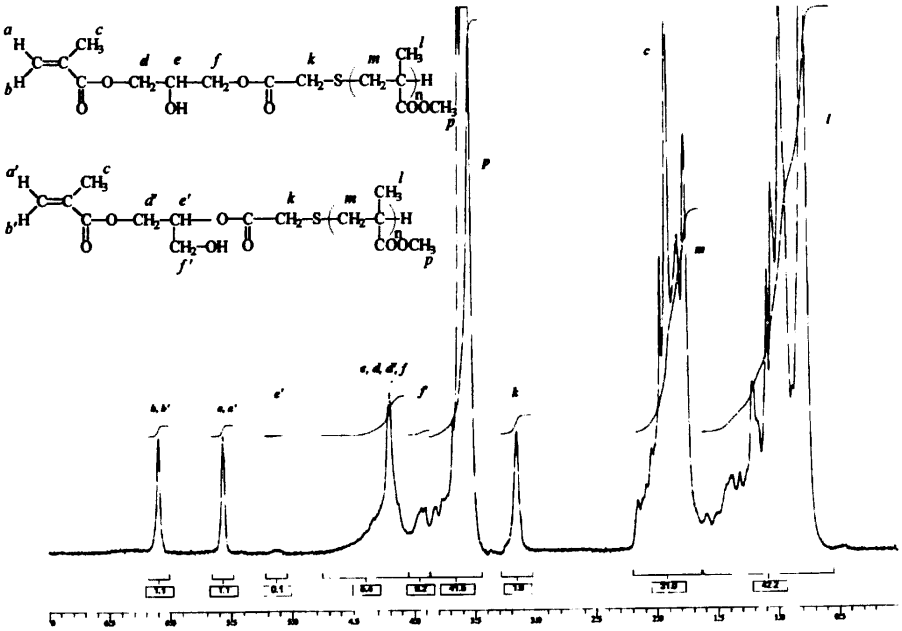


Figure 3 : ^{1}H NMR of PMMA macromonomers

From this ^{1}H NMR study, it is confirmed that products were also obtained via two ways of addition. However, we observed a smaller β addition (10%) than in the model study. This decrease is most probably due to the steric hindrance of the PMMA telomer.

Conclusion

Our work using chromium salt as catalyst allows to prepare PMMA macromonomer via reaction of PMMA telomer carboxylic acid end-groups with GMA at lower temperature (70°C) compared to other works operating with amine salts (140°C).

Furthermore, the ^{1}H NMR study of this work shows that the reaction between GMA and PMMA telomer carboxylic acid end-groups is the result of two ways of addition (α and β).

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References

1. Lehn JM (1996) << Comprehensive Supramolecular Chemistry >>, Pergamon Press
2. Nagasahi Y., Sato Y., Kato M (1997) Macromol. Rapid. Commun. 18 : 827-835
3. Park IJ, Lee SB, Choi CK (1997) Polymer 38(10) : 2523-2527
4. Rempp PF, Franta E (1984) Adv. Polym. Sci. 58
5. Hatada K, Kitayama T, Ute K, Masuda E, Shinozahi T, Yamamoto M, (1989) Polym. Bull. 21 : 165
6. Xie HQ, Wu XD, Guo JS (1994) J. of Appl. Polym. Sci. 54 : 1079-1086
7. Ohashi M, Kotera N (1994) Macromol. Rapid. Commun. 15 : 713-717
8. Rempp PF, Masson P, Chaumont P, Franta E (1985) Makromol. Chem. Suppl. 13 : 47
9. Witroushi R, Bandermann F (1989) Makromol. Chem. 190(9) : 2173
10. Heitz T, Welster OW (1991) Makromol. Chem. 192(10) : 2463
11. Radse W, Mueller AHE (1996) Makromol. Symp. 101 : 19-27
12. Shen W, Jim HM (1992) Makromol. Chem. 193 : 743-748
13. Zink MO, Colombani D, Chaumont P (1997) Eur. Polym. J. 33(9) : 1433-1440
14. Reghunadhan Nair CP, Chaumont P, Charmot D (1995) J. of Polym. Sci. 33 : 2773-2786
15. Krstina J, Moad CL, Moad G, Rizzardo E (1996) Makromol. Symp. 111 : 13-23
16. Haddleton D, Maloney DR, Suddaly KG, Clarbe A (1997) 38(25) : 6207-6217
17. Moad CL, Moad G, Rizzardo E, Thang SH (1996) Macromolecules 29 : 7717-7726
18. Yamada B, Otsu T (1990) Makromol. Chem. Rapid. Commun. 11 : 513-518
19. Ito K, Hashizuka H, Yamashita Y (1977) Macromolecules 10 : 821
20. Yamashita Y, Chujo Y, Kobayashi H, Hawakami H (1981) Polym. Bull. 5 : 361
21. Chen GF, Jones FN (1991) Macromolecules 24 : 2151
22. Ishizu K, Ono T, Fubutomi T (1987) J. Polym. Sci. Polym. Lett. Ed. 25 : 131
23. Ito K, Usami N, Yamashita Y (1980) Macromolecules 13, 216
24. Yamashita Y, Tsukahara Y, Ito K, Okada K, Tajima Y (1981) Polym. Bull.5,335
25. Mc Cord EF, Anton WL, Wilczek L, Ittel SD, Nelson LTJ, Raffell KD (1994) Macromol. Symp. 86 : 47-64
26. Loubat C, Boutevin B (2000) (under press in Makromol. Chem.)
27. Mayo FR (1943) J. Am. Chem. Soc. 65 : 2324
28. Ohtani H, Luo YF, Nakashima Y, Tsukahara Y, Tsuge S (1994) Anal. Chem. 66 : 1438-1443
29. Tsukahara Y, Nakanishi Y, Yamashita Y, Ohtani H, Nakashima Y, Luo YF, Ando T, Tsuge S (1991) Macromolecules 24 : 2493-2497
30. Uri N (1971) Br. Polym. J. 3 : 138-144