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The synthesis of poly(methyl methacrylate) containing crown ether units using macroazoinitiators and its cation binding properties

Umit Tunca and Yusuf Yagci*

Istanbul Technical University, Department of Chemistry, Maslak, TR-80626 Istanbul, Turkey

SUMMARY

Poly(methyl methacrylate) having crown ether units was prepared by using polyazoamides as initiators. The complexing properties of the obtained polymers towards metals were reported. The crown ether content of the polymer had influence upon the complexing capability.

INTRODUCTION

Crown ethers which have the ability to bind metal cations in their cavities are of increasing interest [1,2]. The incorporation of crown ether units can induce complexing in the polymer. A number of studies on combining crown ether structures with polymers have been reported [3-14]. Recently we have synthesized a macroazonitiator for the synthesis of polymers with crown ether units by solution [15] and interfacial [16] polycondensation reaction. The latter provided complexation of the crown ether moiety before the polymer was synthesized, and the crown ether complex probably acted also as a phase transfer catalyst between water and the organic phase. The resulting polyamide is a useful initiator for free radical polymerization. More recently, we have prepared copolyamides containing crown ether moities and the desired amount of thermolabile azo groups[17].

Here we wish to report the utilization of polyazoamides as free radical initiator by which poly(methyl methacrylate) (PMMA) having various segment length of the crown ether moiety can be prepared. The extraction of some metal cations by the resultant PMMA was also examined.

EXPERIMENTAL

Materials and Instruments

The preparation of polyazoamides was described in detail previously [17]. Methyl methacrylate (MMA) was washed with 5 % aqueous NaOH and water, dried over $CaCl_2$ and finally distilled over CaH_2 under reduced pressure.

^{1}H-NMR spectra were recorded on a Brucker NMR (200 mHz) in $CDCl_3$ with TMS as internal standard. UV spectra were obtained with a Shimadzu UV 150-02 instrument. GPC chromatograms were obtained from a Knauer M64 system with methyl ethyl ketone as eluent and a flow rate of 1 ml/min. Molecular weights were calculated according to polystyrene standard samples.

*To whom offprint requests should be sent

Polymerization of MMA

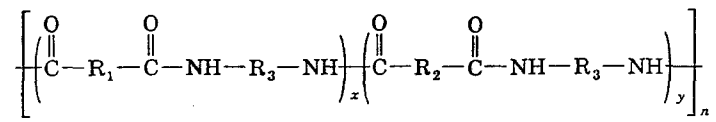
Appropriate solutions of polyazomides and MMA in DMF were degassed and sealed in the usual manner. After heating at 70 °C, polymers were recovered by precipitation into methanol. They were purified by reprecitation from methanol before used in the extraction of metal ions.

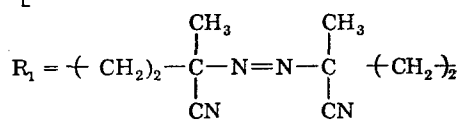
Extraction of Metal Picrates

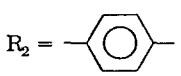
Appropriate aqueous solitions were prepared from given amount of metal hydroxide and picric acid in water. The crown ether containing PMMA was dissolved in methylene chloride. Equal volumes of each solution were mixed and shaken at room temperature overnight. The concentration of picrate anion remaining in the aqueous phase was determined by UV measurement at 357 nm.

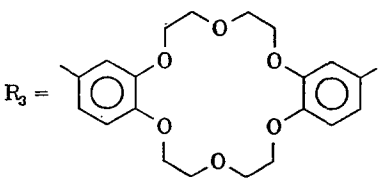
RESULTS AND DISCUSSION

Two types of polyazoamides having the following structures were used as initiators containing crown ether moieties for the polymerization of MMA. The results are shown in Table 1.









PAA-1; x/x+y =1

PAA-2; x/x+y=0.6

Table 1
Synthesis of Crown Ether(CE) Containing PMMA by Using Polyazoamides (PAA) as Initiator at 70 °C

PAA (g/l)	MMA (mol/l)	Time (min)	Conv. (%)	$\overline{M}_n$ x10^{-3})a (g/l)	Number. of CE per macromol.)b
PAA-1(10.5)	7.0	60	8	54	22.6
PAA-2(8.0)	4.7	120	25	48	31.2

a Calculated by GPC
b Calculated by ^{1}H-NMR spectra

The obtained PMMA has crown ether moities and the number of crown ether units per macromolecular chain can be contralled by the amount of -N=N- units in the main chain of the initial polyazoamide. The extraction of picrate salts by the obtained polymers was tested to investigate their cation binding properties.The fraction of picrate salts extracted by the polymers into a methylene choride phase is shown in Table 2. For all alkali and alkaline earth metal cations the polymer with higher crown ether content, namely PMMA-1, showed a higher extraction capability.

Table 2
Solvent extraction of metal picrates by PMMAs[a]

PMMA	Picrate salt extracted (%)				
	K^+	Na^+	Cs^+	Ca^{++}	Ba^{++}
PMMA-1[b]	15.2	8.4	10.0	10.1	16.0
PMMA-2[c]	39.9	18.2	42.1		34.4

a CH_2Cl_2/H_2O (1/1,v/v), [Metal hydroxide] = 5 x 10^{-2} mol/l
b [Crown units] = 2.1 x 10^{-3} mol/l, [Picric acid] = 7 x 10^{-5} mol/l
c [Crown units] = 10^{-2} mol/l, [Picric acid] = 2.3 x 10^{-5} mol/l

For PMMA-1, the order of alkali cation selectivity was $K^+ > Cs^+ > Na^+$. PMMA-2, however showed cation selectivity in the order of $Cs^+ > K^+ > Na^+$, which is the order reported [18] for polymers with 18-crown-6 pendant groups. It is known [18] that the effective cation binding properties of polymers with crown ethers are due essentially to a cooperative action of pendant groups in the polymer chain. It should be pointed out that the cooperative action of crown ether units in the main chain of a polymer can only be probable by the entanglement of chains by which the cation is sandwiched between two crown units situated on the same or different chains as depicted below.

CE = Crown Ether

Notably, the importance of this behaviour depends on the crown ether content of the polymer as was observed for PMMA-2. In this respect,it is worth mentioning the work of Shah et al [19] who reported the competetive formation of inter- and intramolecular 2:1 crown-cation complexes.They showed that at low crown concentration, intramolecular complexes can form when crown ligands are separated by less than four repeating units.

Polymers, containing crown ether units in the main chain, synthesized by means of macroazoinitiators may be useful for polymer-metal complexation or metal-extraction.

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REFERENCES

1. G.W.Gokel, D.M.Galli, C.Minganti and L.Echegogen J.Am.Chem.Soc.,105,6786(1983)
2. Y.Takeda in Topics in Current Chemistry, Host Guest Complex Chemistry III, F.Vogtle and E.Weber, Eds.,Spring-Verlag Berling,1984
3. E.Schchori and J.J.Grodzinski, J.Appl.Polym.Sci.,20,1665(1976)
4. A.J.Varma, T.Majevicz and J.Smid,J.Polym.Sci.,Polym.Chem.Ed.,17,1573(1979)
5. K.Yagi, J.A.Ruiz and M.C.Sanchez Makromol.Chem.,Rapid Commun.,1,263(1980)
6. K.Kimura, H.Tamura, T.Maeda and T.Shono, Polym.Bull. 1,403(1979)
7. K.Kimura, M.Yoshinaga, S.Kitazawa and T.Shono, J.Polym.Sci.,Polym.Chem.Ed. 21,2777(1983)
8. J.I.Anzai, Y.Sakata, Y.Suzuki, A.Ueno and T.Osa, J.Polym.Sci.,Polym.Chem. Ed.,21,855(1983)
9. S.Shinkai, H.Kinda, M.Ishihara and O.Manabe, J.Polym.Sci.,Polym.Chem.Ed., 21,3525(1983)
10. M.Shirai, T.Orikaka and M.Tanaka, J.Polym.Sci.,Polym.Chem.Ed.,23,463(1985)
11. M.Shirai, A.Ueda and M.Tanaka, Makromol.Chem.186,2519(1985)
12. T.Kakuchi and K.Yokota, Makromol.Chem.,Rapid Commun. 6,551(1985)
13. T.Kakuchi, O.Kobayashi, D.Nakaya and K.Yokota, Polym.J.,21,649(1989)
14. Y.Chujo, T.Nakamura and Y.Yamashita, J.Polym.Sci.,Polym.Chem.Ed.,28,59(1990)
15. Y.Yagci, U.Tunca and N.Bicak, J.Polym.Sci.,Polym.Let.Ed.,24,49(1986)
16. Y.Yagci, U.Tunca and N.Bicak, J.Polym.Sci.,Polym.Let.Ed.,24,491(1986)
17. U.Tunca and Y.Yagci J.Polym.Sci.,Polym.Chem.Ed.,28,1721(1990)
18. S.Kopolow, T.E.H.Esch and J.Smid, Macromolecules 6,133(1973)
19. S.C.Shah, S.Kopolow and J.Smid, Polymer 21,188(1980)

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