

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis of Block Copolymers by Redox Macro Initiators

Ismail Çakmak<sup>a</sup>

<sup>a</sup> Department of Science Education, Karadeniz Technical University, TURKEY

**To cite this Article** Çakmak, Ismail(1995) 'Synthesis of Block Copolymers by Redox Macro Initiators', Journal of Macromolecular Science, Part A, 32: 1, 197 – 206

**To link to this Article: DOI:** 10.1080/10601329508020328

**URL:** <http://dx.doi.org/10.1080/10601329508020328>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **SYNTHESIS OF BLOCK COPOLYMERS BY REDOX MACRO INITIATORS**

**İsmail Çakmak**

Karadeniz Technical University, Department of Science  
Education 61335 Söğütli-Trabzon/TURKEY

### **ABSTRACT**

Redox systems in block copolymer synthesis are reviewed, especially those methods that lead to well-defined structures: poly (ethylene oxide), azo, macroazo, peroxy or hydroperoxy redox macro initiators from vinyl monomers.

### **INTRODUCTION**

Block copolymers are polymers in which there are at least two different segments. They have been also considered as macromolecules formed by the chemical combination of two different homopolymers end to end. They have a widespread usage in commercial market as raw materials for surfactants, adhesives, fibers, elastomers, thermoplastics and thermoplastic elastomers.

The synthesis of block copolymer was first carried out by Bolland and Melville[1] via living macro radicals in 1938. However, the industrial importance of block copolymers was recognized after Szwarc et. al. [2] who synthesized well-defined block copolymers via living macro anions in 1956.

Since then, several methods such as free radical, step growth, anionic, cationic, coordination and group transfer polymerizations have been developed to synthesize block copolymers.

The different techniques of synthesis of block copolymers are reviewed by several authors[3]. In recent years beside various synthetic methods redox initiating systems have been successfully used for the synthesis of block copolymers via a radical mechanism[4-6].

Polymerizations initiated by the reaction between an oxidizing and a reducing agent called redox polymerization. The developments in redox polymerization have been reported in many review articles by several authors[7].

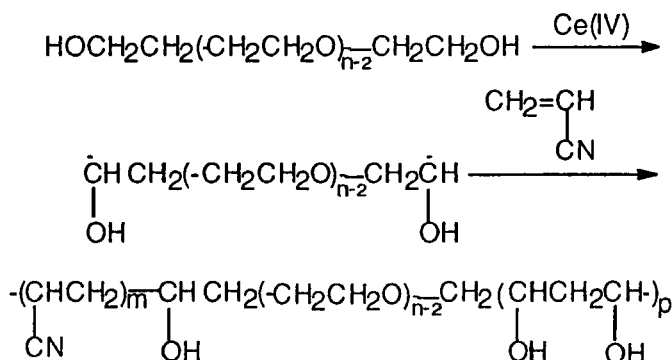
The essence of redox initiation is a reduction-oxidation process. In this process oxidant, i.e., Ce(IV), Mn(III) forms initially a complex by reacting simply organic molecules which then decomposes unimolecularly to produce free radicals that initiates polymerization. Commonly used oxidants are include peroxides, persulfates peroxydiphosphate, the salts of transition metals.

These oxidants form effective redox systems with various reducing agents like alcohols, aldehydes, amines, thiols for the aqueous polymerization of vinyl monomers. The essential feature of components constituting a redox pair for aqueous polymerization is their solubility in water and fairly fast and steady liberation of active radicals.

When a polymeric substrate is used as a redox system in conjunction with an oxidant for the polymerization of vinyl monomers to form block or graft copolymers, the radical generated on the polymer substrate acts as a macro initiator.

### POLY(ETHYLENE OXIDE) REDOX MACRO INITIATORS :

Novitskaya and Konkin[8] have firstly used Ce(IV)-poly(ethylene oxide)(PEO) redox system as macro initiator for the aqueous polymerization of acrylonitrile(AN) to produce ABA type block copolymers. The reaction steps may be represented as follows.

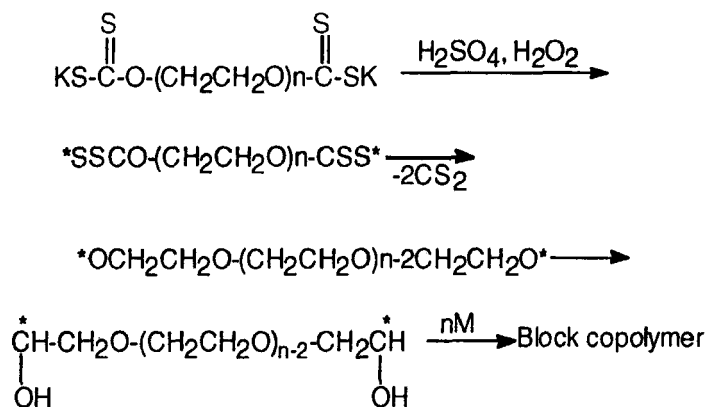


Scheme 1

The authors showed that, when the polymerization is carried out for a short period of time only, homopolymerization of acrylonitrile can be avoided, since it has a lengthy induction period.

Similarly Gomes et. al.[9] have reported the synthesis of the block copolymers of poly(ethylene oxide) and methyl methacrylate. In this case, they have used Ce(IV)/PEO as a redox macro initiator for the polymerization of MMA in 1,4-dioxane solution. The kinetics and characterization of block copolymerization of MMA initiated Ce(IV)/PEO redox system were also studied[10].

ABA type triblock copolymers comprising Poly(ethylene oxide) as the A component and the poly(acrylonitrile), poly(acrylamide) or poly(methyl methacrylate) as the B component were prepared via redox initiation method[11-12]. In aqueous polymerization, these block copolymers were obtained by initiating the polymerization of AN, AAm or MMA with poly(ethylene glycol) in the presence



Scheme 2

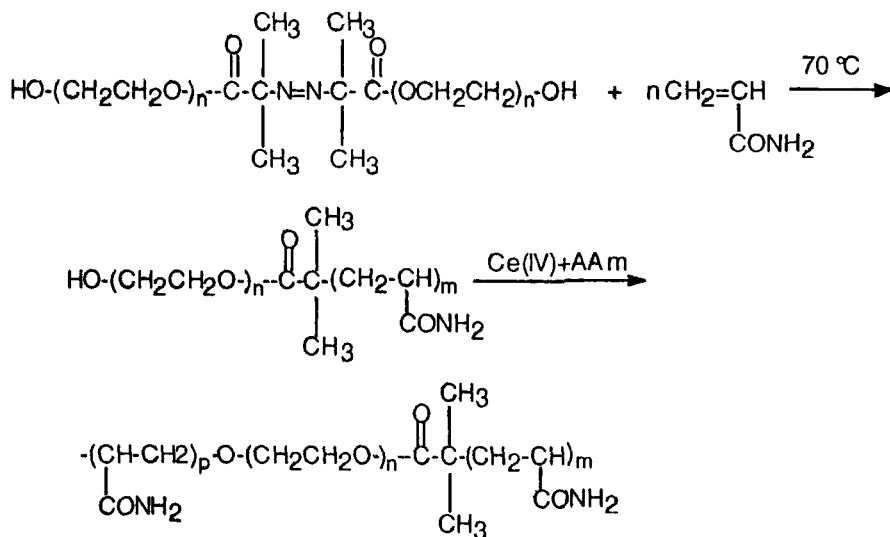
of Mn(III) ions.  $\text{CH}_3\text{COOH}$  and  $\text{H}_2\text{SO}_4$  were added to the reaction medium to increase the stability of the Mn(III) ions. The principal parameters (concentration of reactants, temperature) affecting the synthesis were also examined and the successful blocking has been confirmed by viscosity measurements and spectroscopic methods as well as gel permeation chromatography. Reaction pathways are similar as scheme 1.

The potassium or sodium salt of PEO xanthate with  $\text{H}_2\text{O}_2$  were used in the AN[5,13] and MMA[14] polymerization in sulfuric acid media. The synthesis of block copolymers was carried out in aqueous medium in the presence of  $\text{H}_2\text{SO}_4$  using PEO-xanthate as reducing agent and  $\text{H}_2\text{O}_2$  as oxidizer. The oxidation of xanthate ions results in the formation of active center on sulfur atoms, which then undergo isomerization, bringing about active centers on carbon atoms[5,15].

Yağcı et al. [16] obtained water soluble poly(acrylamide)s with high molecular weight via a two step procedure. In this procedure, aqueous polymerization of acrylamide (AAM) was initiated by using a macro-azo-initiator to yield hydroxyl terminated PAAM. When these polymers are used as organic reducing agents in conjunction with ceric salt, free radicals are formed by a transfer of an electron. Polymeric radicals thus formed are capable of initiating the polymerization of AAM giving rise to chain extension and consequently high molecular weight PAAM. The water-soluble block copolymers obtained at various conditions were tested in the flocculation of suspension of tincal concentrate and showed good flocculating properties.

The overall process may be represented as shown in scheme 3.

Deodecyl poly(ethylene oxide)(DDPEO) was used with ceric ammonium nitrate as a macro redox catalyst for emulsion polymerization of methyl methacrylate to yield AB type block copolymers. In this process, DDPEO also acted as the emulsifying agent[17-18].



Scheme3

### AZO GROUP CONTAINING REDOX MACRO INITIATORS

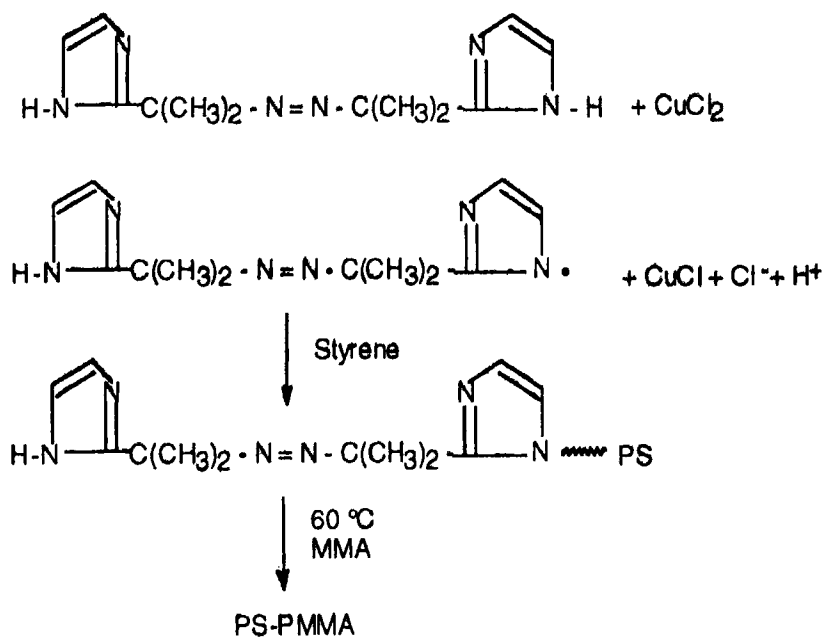
Bifunctional initiator systems that are not based on radical decomposition but include a functional azo compound are an excellent starting material to introduce the azo group in the middle of the polymer chain[3(J)]. Yađcy et. al.[4] firstly used ceric ammonium nitrate in combination with 4,4'-azobis(4-cyanopentanol) as redox initiator for the polymerization of acrylamide to produce poly(acrylamide) having one azo group in the main chain. The pre polymer was used to initiate the thermal polymerization of styrene by a free radical mechanism after eliminating  $\text{N}_2$  to obtain acrylamide-styrene block copolymers.

The radical polymerization of styrene in the presence of 2,2'-azobis [2-(imidazolin-2-yl) propane] dihydrochloride and  $\text{CuCl}_2$  as redox initiator yielded polystyrene having several azo groups since chain termination occurred by radical combination[19]. This macro-azo-initiator was then used for the thermal radical polymerization of methyl methacrylate to produce styrene-methyl methacrylate block copolymers.

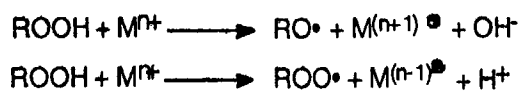
ABCBA type block copolymers were synthesized[6,20-21] by the combination of redox and thermal polymerization of vinyl monomers using poly(ethylene glycol) having azo and hydroxyl functions with  $\text{Ce(IV)}$  or  $\text{Mn(III)}$ .

### HYDROPEROXIDE OR PEROXIDE REDOX MACRO INITIATORS

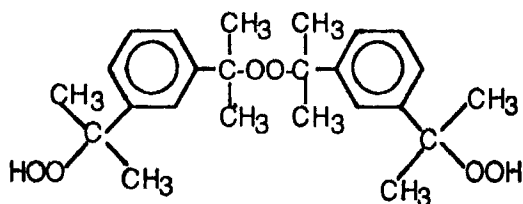
Hydroperoxides in the presence of a metal ion may decompose in either of two ways, generating free radicals as depicted below[7(a)].



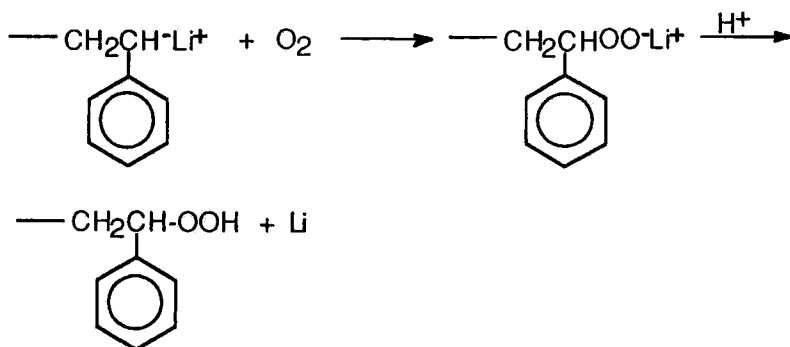
Scheme 4



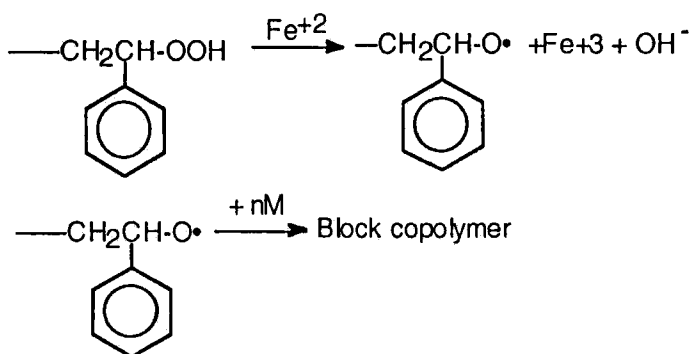
Scheme 5



Scheme 6



Scheme 7



Scheme 8

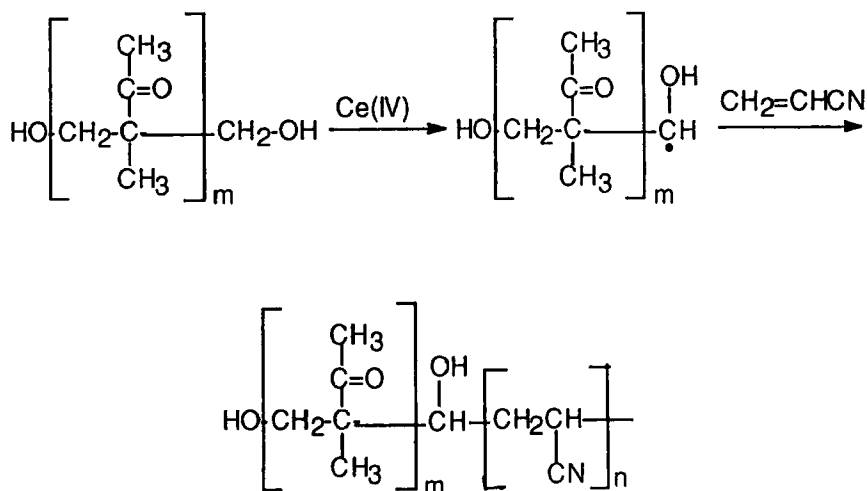
The use of an initiator having two initiating centers of different reactivities such as bis(m-2-hydroperoxy-2-propyl-cumyl) peroxide, has allowed poly(methyl methacrylate-*b*-styrene) to be prepared[22].

The hydroperoxy groups initiated polymerization of MMA at low temperature in the presence of  $\text{OsO}_4$ , and subsequently the PMMA containing peroxy group was used to initiate the styrene polymerization by thermal dissociation of the peroxy groups.

Polymers containing hydroperoxy groups at chain ends with  $\text{Fe}^{+2}$  were used as a redox macro initiators for the block copolymerization of vinyl monomers[23-29].

Catula et. al.[30-31] have prepared the hydroperoxide terminated poly(styrene) by a reaction sequence in scheme 7.

Reacting polymeric hydroperoxide with ferrous sulfate in the presence of a second monomer afforded block copolymers.



Scheme 9

Hazer et. al.[32] were used a macro-azo-peroxy initiator together with 3,6,9-triazoundecane-1,11-diamine as a macro redox initiator in the polymerization of MMA and they obtained PEO-PMMA block copolymers having azo group in the main chain. Thermal decomposition these polymers in the presence of second monomer gave ABCBA type multiphase block copolymers.

Block copolymers containing poly(vinyl chloride) were prepared by redox polymerizing vinyl chloride an optionally comonomers in the presence of the peroxides  $\text{HO}(\text{CR}_1\text{R}_2\text{O}_2\text{R}_3\text{R}_4\text{CO}_2\text{H}$  ( $\text{R}_{1-4}=\text{H}$  or alkyl groups) to give peroxides having terminal vinyl chloride polymers and the block copolymerizing with comonomers by thermal decomposition of the peroxides[33].

#### THE OTHER REDOX MACRO INITIATORS

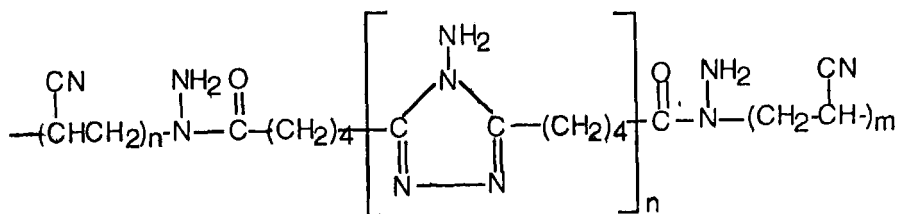
Akar et. al.[34] were polymerized acrylonitrile in the presence of Ce(IV) salts and ketonic resin such as methyl ethyl ketone/formaldehyde or cyclohexanone/formaldehyde to yield the block copolymer of ketonic resin-poly(acrylonitrile).

Mn(III) and poly(acrylamide) having carboxyl groups were used as a macro redox initiator for the block copolymerization of acrylonitrile[35].

Redox reaction between the thiol group at one end of poly(vinyl alcohol) and potassium bromate initiated of several monomers in water, yielding block copolymers having the poly(vinyl alcohol) as one component[36]. The block copolymers obtained showed behavior obviously different from the blend systems of PVA and corresponding homopolymers.

The redox system ferric salt/acyl hydrazide has been used to obtain a poly(aminotriazole-b-acrylonitrile) block copolymer[37] having the structure:





Scheme 10

The formation of free radicals by the reaction of terminal acyl hydrazide groups of poly(aminotriazole)  $\text{RCONHNH}_2$  and  $\text{Fe(III)}$ , may be represented as follows:



Guilbault and Brooks[38] reported the preparation of block copolymers by the reaction of hydroxyl-terminated poly(vinyl pyrrolidone) with methyl methacrylate in the presence of ceric ammonium nitrate. A patent was also issued to Guilbault[39] for similar polymerization reactions utilizing water soluble monomers.

## CONCLUSION

The synthesis of block copolymers by redox systems exerts a number of technical and theoretical advantages over the other methods. Because of applicability at low temperatures, side reactions leading to formation of homopolymers are minimized. The redox systems used in block copolymer synthesis utilized in present review article.

## REFERENCES

1. J.H. Bolland and H.W. Melville, Proceedings of the First Rubber Tech. Conf., London, W. Heffer, P. 239(1938) CA 32, 8396g(1938).
2. M. Szwarc, M. Levy, R. Milkovich, J. Am. Chem. Soc., 78, 2656(1956).
3. a) D.C. Allport, W.H. Janes, Block Copolymers, Applied Science Publishers Ltd., London 1973.
- b) B. Hazer, Synthesis and Characterization of Block Copolymers, In Handbook of Polymer Science and Technology, Vol.1(Ed. N.P. Cheremissinoff), pp. 133-176.
- c) O. Nuyken, R. Weidner, Adv. Polym. Sci., 73/74, 1471(1988).
- d) Y. Yağcı, W. Schanabel, Prog. Polym. Sci., 15, 551(1990).
- e) R. Jerome, T. Tayt, T. Quhadi, Prog. Polym. Sci., 10, 871(1984).

- f) M.J.M. Abadie, D. Ourahmoque, *Br. Polym. J.*, 19, 247(1987).
- g) M.J. Stewart, Transformation Reactions, In *New Methods of Polymer Synthesis*. (Ed. J.R. Ebdon) pp. 107-137. Blackie Academic and Professional, Glasgow, UK. 1993.
- h) Y. Yağcı, M.K. Mishra, *Macroinitiators for Chain Polymerization, In Macromolecular Design; Concept and Practice* (Ed. M.K. Mishra), pp. 229-264. Polymer Frontiers Int. Inc. New York, USA, 1994.
- i) A. Udea, S. Nagai, *Macroinitiators Including syntheses and applications of block copolymers derived therefrom*, *ibid.*, pp.265-312.
- J) O. Nuyken, B. Voit, *Polymeric Azo initiators*, *Ibid.*, pp.313-358.
- k) M. Okada, *Block and Graft Copolymers by Ring Opening polymerization using various macroinitiators*. *Ibid.*, pp.359-389.
- l) Y. Yağcı, M.K. Mishra, *Macroinitiators in multimode polymerization*, *Ibid.*, pp.391-429.
- m) M.K. Mishra, Y. Yağcı, *An Introduction to Macroinimer, Macroiniter, Macroinifer.*, *Ibid.*, pp.499-506.
- n) K. QiU, *Gadeng Xucxiao Huaxue Xucbau* 12,133(1991). CA, 183979m(1991).
4. Ü. Tunca, İ.E. Serhatlı, Y. Yağcı, *Polym. Bull.*(Berlin), 22, 483(1989).
5. T. Wodka, *J. Appl. Polym. Sci.*, 37, 581(1989).
6. İ. Çakmak, B. Hazer, Y. Yağcı, *Eur. Polym. J.*, 27, 101(1991).
7. a) G.S. Mishra, U.D.N. Bajpai, *Prog. Polym.Sci.*, 8, 61(1982).  
b) S. Rubio, B. Serre, J. Sledz, F. Schue, G.C. Letourneux, *J. Macromol. Sci. Rev. Macromol.Chem.*, C19(2), 175(1980).  
c) M.K. Mishra, *J. Macromol. Sci. Rev. Macromol. Chem.*, C19(2), 193(1980).  
d) M.K. Mishra, *J. Macromol. Sci. Rev. Macromol.Chem.*, C22(3), 471(1982).
8. (a) M.A. Novitskaya, A.A. Konkin, *Vysokomol. Soediniya*, 7(10), 1719(1965). CA, 64, 3710f(1966).  
(b) A. A. Konkin, *Prezemysl Chem.*, 45(3), 233(1966). CA, 65, 15664a(1966).
9. A.S. Gomes, F.M.B. Coutinho, J.R.D. Marinho, *J. Polym. Sci., Part C: Polym. Lett.*, 25, 237(1987).
10. F.M.B. Coutinho, C.R.G. Furtado, *Eur. Polym. J.*, 30,113(1994).
11. İ. Çakmak, *Angew. Makromol. Chem.*, 211, 53(1994).
12. İ. Çakmak, *Preparation of multiphase block copolymers by redox polymerization process.3*, *Angew. Makromol. Chem.*, 1994 (In press).
13. R. Kwiatkowski, A. Wlochowicz, T. Wodka, *Angew. Makromol. Chem.* 180, 145(1990).
14. İ. Çakmak, *Polymerization of methyl methacrylate initiated by the redox system H<sub>2</sub>O<sub>2</sub> -poly(ethylene oxide) with xanthate groups.*, *Eur. Polym. J.*(1994) (in press).
15. K. Dimov, P.Pavlov, *J. Polym. Sci., Polym. Chem.*, A1, 2775(1969).
16. A.T. Erciyes, M. Erim, B. Hazer, Y. Yağcı, *Angew. Makromol. Chem.*, 200, 163(1992).
17. F.M.B. Coutinho, C.R.G. Furtado, *Mem. Simp. Lationam polim.*, 3rd, 63-74(1992)., CA, 192346s(1993).

18. F.M.B. Coutinho, C.R.G. Furtado, *Eur. Polym.J.*, 28, 1111(1992).
19. H. Narita, H. Kinoshita, T. Araki, *J. Polym. Sci., Part A: Polym. Chem.*, 30, 333(1992).
20. B. Hazer, İ. Çakmak, S. Denizligil, Y. Yağcı, *Angew. Makromol. Chem.*, 195, 121(1992).
21. İ. Çakmak, Preparation of multiphase block copolymers by redox polymerization process.4., *Angew. Makromol. Chem.*, 1994 (in press).
22. G.H. Twigg, J.L.B. Benton, The Distillers Co. Ltd., *British Pat.*, 857,145 29.12.1960.
23. J.A. Hick, H.W. McIwille, *J. Polym. Sci.*, 12, 461(1954).
24. P. Molyneux, *Makromol. Chem.*, 37,165(1960).
25. G.M. Burnelt, P. Meares, C. Paton, *Trans. Faraday. Soc.*, 58,723 (1962).
26. R.J. Orr, H.L. Williams, *J. Am. Chem. Soc.*, 79, 3137(1957).
27. J.R. Urwin, *J. Polym. Sci.*, 27, 580(1958).
28. P. Molyneux, *Makromol. Chem.*, 43, 31(1961).
29. S. Kobayashi, F. Ide, K. Nakasuka, *Chem. High. Polymers(Japan)*, 24, 17(1967).
30. R. Reeb, Y. Vinchon, G. Riess, J.M. Catula, J. Borassas, *J. Bull. Soc. Chim. France.*, 11-12, 2717(1975).
31. J.M. Catula, G. Riess, J. Brossas, *Makromol. Chem.*, 178, 1249(1979).
32. B. Hazer, A. Ayas, N. Beşirli, N. Saltık, B.M. Baysal, *Makromol. Chem.* 190, 1987(1989).
33. H. Nebekura, T. Shimizu, Kanegfuchi Chem. Ind. Co. Ltd., *Jpn. Kokai Tokyo Koho JP.*, [90,129,212] (1990) CA, 22, 153269w(1990).
34. A. Akar, O. Galioğlu, A. Göçmen, A.S. Saraç, *J. Appl. Polym. Sci.*, 39, 1657(1990).
35. İ. Çakmak, *Macromol. Reports.*, A31(1/2), 85(1994).
36. K. Tereda, T. Sato, H. Maruyama, J. Yamauchi, T. Okaga, *Kobunshi Ronbunshu*, 49(11), 885(1992).
37. Y. Iwakura, M. Kakajima, E. Kitani, *Chem. High. Polymers(Japan)*, 19, 161(1962).
38. L.J. Guilbault, T.W. Brooks, *J. Macromol. Sci. Chem.*, A7, 1581(1973).
39. L.J. Guilbault, *U.S. Patent*, 3,907,927(1975).