韓·日 共同 심포지엄 發表論文 揭載

Macromer Technology

Iwhan Cho

Korea Advanced Institute of Science
Seoul 131, Korea

The term "macromolecular monomer" was first used in 1972 by Milkovich et al.[1] of Corn Product Corp., International to denote various polymers of wide molecular weight range with polymerizable terminal functions such as olefinic, acryl or epoxy groups. These macromolecular monomers were copolymerized with other usual monomers to prepare graft copolymers. The word "Macromers" are supposedly an acronym of macromolecular monomers and used by CPC, International to register their commercial macromolecular monomers.

Since the introduction the word "macromer" has been gradually applied without clear categorial definition by polymer chemists to those polymerizable high molecular weight compounds[2]. This conceptual development has lead the scope of macromers to interphase considerably with that of wide variety of the materials indiscriminately called "prepolymers". Under this circumstances proposed is to extend the meaning of macromer and to use the term "macromer" with the following definition: "A macromer is a polymer, in its broad sense, with the defined reactive functions at the ends and/or on the chain, which can constitute a building block of the final polymers of certain values via suitable chain-extending reactions."

With this definition the poly (oxytetramethylene) glycol of molecular weight 3,000 is a typical macromer and it becomes then obvious that polyurethane technology can be classified as a part of macromer technology. Macromer technology should cover also other polymer-related areas such as telechelic polymers[3], functionally terminated oligomers[4], liquid polymers[5] etc.

Classification

Because of the possible diversity in its function and structure macromers can be classified in many different ways.

Classification according to the chain-extending reaction

a) Addition macromers: To be called an addition macromer is a macromer with the functional group(s) which is reactive under addition polymerization conditions, e.g., poly (oxyethylene) dimethacrylate[6], polystyrene acrylate[1] etc.

b) Condensation macromers: To be grouped in this category are those macromers with the functional groups which are reactive towards condensation polymerization reactions. A large number of commercially available macromers (mostly for polyurethane formulations) belong to this class, e.g., PEG, PPG, PTMG, polybutadiene diol[7], poly(oxypropylene) diamine[8], polybutadiene dicarboxylic acid[7], thiol-terminated liquid polymers[5], ethylene diamine-initiated polymerization products[13] of ethylene oxide or propylene oxide, and others.

c) Ring-opening macromers: Ring-opening macromers are the macromers with reactive cyclic functional groups which can ring-open

to polymerize, e.g., poly(oxyethylene) diepoxide[9], polystyrene epoxide[1], polybutadiene diepoxide[10], polybutadiene diaziridine[11] etc.

Preparation of Macromers

1. Living Polymer Reactions

Living polymers of various chain structures and different molecular weights can be consi dered as macromers in themselves: macromers in situ. However upon the reactions with different types of compounds the living polymers can provide macromers of wide variety of functions. The versatility of this method was well demonstrated early by Szwarc et al.[14] and others. The addition of carbon dioxide or ethylene oxide to living polystyryl anions produce polystyrenes of controlled molecular weight with terminal carboxyl or hydroxyl groups on acidification.

2. Radical Polymerization Method

When a radical polymerization proceeds with bimolecular termination, the application of suitably functionalized radical initiators can provide macromers with the functions at the two chain ends. 4,4′-Azo-bis (4-cyanovaleric acid)[15] and 4,4′-azo-bis (4-cyano-n-amyl alcohol)[16] can be applied to prepare polybutadiene macromers with terminal carboxyl and hydroxyl groups.

In the preparation of carboxyl-terminated polybutadiene, dithiodibutyric acid[15] can be used to regulate the molecular weights.

3. Condensation Polymerization Method

Polyester diols such as hydroxyl-terminated poly(tetramethylene) adipate for polyurethane formulations are classic examples in that condensation polymerization technique is successfully applied for the macromer preparation. Amine-terminated polyamides[17] and phenol-terminated polysulfones[18] are other examples. In principle, all the condensation polymerization products at certain conversion level may be considered as macromers with two different functional groups statistically distributed at two chain ends.

4. Ring-Opening Polymerization Method

This method is somewhat analogous to addition and condensation polymerization methods. Diol-initiated polymerizations of ethylene oxide, propylene oxide and caprolactone should lead to the corresponding macromeric polyethylene glycol, polypropylene glycol and polycaprolactone diol.

5. Polymer Degradation Method

Among the possible preparative methods for macromers this is least studied and less applicable method. Degradation reactions are often ill defined and difficult to run for preparative purposes. However macromers of certain structures are possibly prepared only by this particular method.

A good example is macromeric polyisobutylenes. Carboxyl-terminated polyisobutylene[19] macromers have been prepared by ozonolysis of isobutylene-isoprene copolymers. An interesting possible application of this method is the production of useful macromers by the degradation of waste polymers.

6. Terminal Group Reactions

Often it is necessary to convert one kind of macromeric functions to another kind usually to improve the reactivities. Commercially available poly(oxypropylene) diamine, Jeffamines^R of Jefferson Chemical Co., is a good example in that poly(oxypropylene) glycol is aminated in the presence of a catalyst to poly(oxypro-

pylene) diamine. An isocyanate-terminated prepolymer prepared by reacting diisocyanate with a polymer polyol is another example of successful application of terminal group reactions to enhance the reactivity of a macromer.

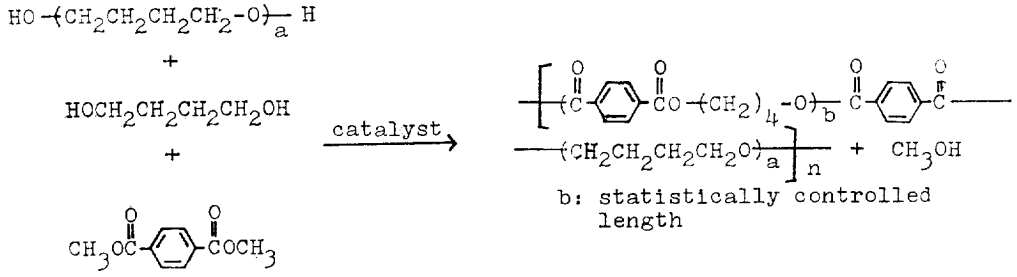
Polymer Syntheses

With wide variety of chain structures and reactive functions available to deploy the macromer approach, with proper adaptation of modern synthetic tools, can be only the accessible route to the polymers of unusual structural constitution, which are considered otherwise formidable. Certain structural combinations of polymer chains of different synthetic origins and of extremely incompatible properties are difficult to achieve. Various block copolymers such as block copolymers of polybutadiene with polyamide, graft and block copolymers of EPR with polyesters, block copolymers of elastomeric silicones with high temperature engineering plastics are good examples. Only the probable approach to those difficult-to-synthesize polymer structures are by the suitable manipulations of synthetic sequences based on macromers.

In the present section some recent development in macromer-based polymer syntheses and their technical implications are to be reviewed. Traditional polyurethane technology and living polymer-bases syntheses are to be left out for other abundant published literatures.

1. Multiblock Copolymers $\{(A)_a—(B)_b\}_n$

Preparations of random multiblock copolymers based on macromers are best illustrated by those of poly(ester-ether)block copolymers. The random multiblock copolymers which can be prepared by cocondensing macromeric poly (oxyalkylene) glycol and monomeric diols such as ethylene glycol and butylene glycol with dimethyl terephthalate are good thermoplastic elastomers and have been well investigated. One commercial product of this type is DuPont's Hytrel[R] which are supposedly the condensates of poly(oxytetramethylene) glycol and butylene glycol with dimethyl terephthalate in different molar rations.



The properties of two grades of Hytrel are compared with those of polyurethane and nylon 11 in Table I. Hytrel thermoplastic elastomers are claimed to have good melt-flow behaviors for various molding processes.

Table I. Properties of Hytrels as Compared to Polyurethane and Nylon 11[20]

Property	Hytrel 53D	Hytrel 63D	Thermoplastic ester urethane	Plasticized nylon 11
Tensile at break	5030	6250	5200	8400
Elongation at break	490	605	435	365
100% modulus (psi)	2475	2160	2000	3810
300% modulus (psi)	3530	2680	3680	6125

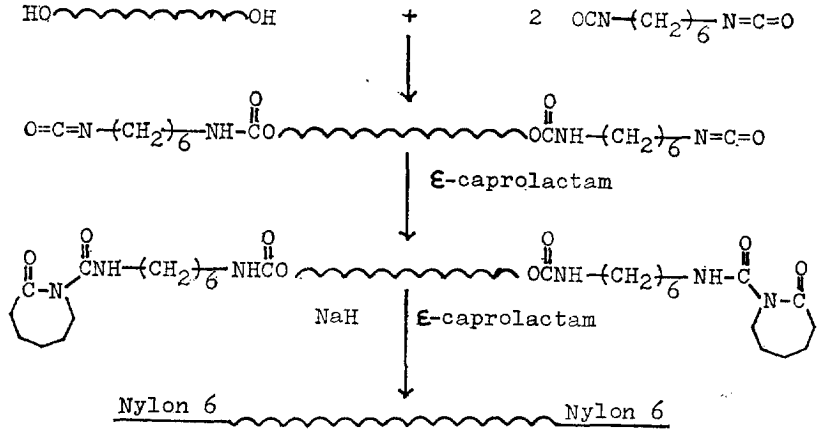
2. ABA Triblock Copolymers

The most widely investigated among various block copolymers are the triblock copolymers of ABA type. These ABA triblock copolymers with hard A and soft B segments show unigue thermoplastic elastomer properties and Kratons^{R} of Shell Co. are good examples.

Macromeric approach to the synthesis of ABA triblock copolymers can take two routes: 1. Polymerization of a monomers by two terminal initiating groups of a macromer i. e., macromeric initiator polymerization.

2. Terminal group interaction of monofunc tional[12] macromer A and difunctional macromer B.

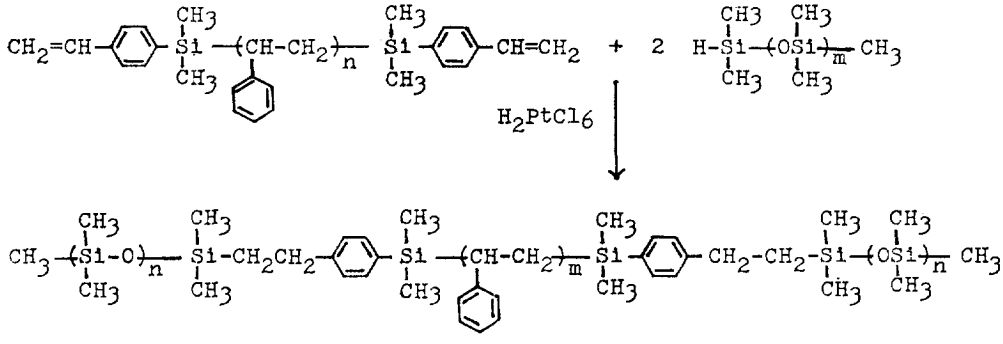
There numerous reported instances wherein certain monomers are polymerized by activated terminal groups of macromers. A good example is anionic polymerization of ε-caprolactam by isocyanate-terminated macromers as an initiator[21].



Numerous other random multiblock copolymers such as polycarbonate, polyamide etc. have been also reported and their possible applications as specialty materials have been suggested.

Another similar example is so-called cationic polymerization of ε-caprolactam by amine-terminated macromers[22] in the presence of phosphoric acid.

Various vinyl polymerization such as polymerization of acrylonitrile by sodium derivative of macromeric glycols[23], radical polymerization of vinyl monomers by peroxycarbamate-terminated macromers[24], vinyl polymerizations by the radicals formed upon the reaction of Ce^{4+} with macromeric glycols[25] etc. have been re-



ported. However in every case the product copolymer was heavily contaminated with vinyl homopolymers. Furthermore if the mode of termination reaction is by coupling rather than exclusive disproportionation, the product block copolymers would not have been expected ABA triblock structures.

An interesting reported case wherein ABA triblock copolymers were prepared by terminal group interactions of two macromers is the synthesis of siloxane-styrene siloxane triblock copolymers[26].

3. Graft Copolymers

The macromers with one terminal olefinic polymerizable group such as those described by Milkovich et al.[1] can be copolymerized with common monomers to obtain graft copolymers of well controlled graft length and grafting frequency. In theory many types of polymerizable functions can be introduced to the monofunctional[12] macromers and various graft copolymers can be synthesized. Poly (ethylene glycol monomethyl ether) of different molecular weights can be reacted with acrylic or methacrylic acid to convert raidcally polymerizable macromeric acrylates which can be copolymerized with acrylonitrile to improve hydrophilic properties of acrylic fibers[27].

4. Other Applications

In principle many other polymeric materials of novel structures can be constructed by the proper applications of macromer techniques.

One good example is construction of three dimensional networks of controlled moiety[28] by gelation of proper, radical-structured macromers.

Conclusion

Polymer-synthetic practice which employs, one way or another, macromer, technique has been steadily gaining its potential as a synthetic tool to construct the polymer structures of unique material properties. And the introduction of a new term, macromer as defined and proposed in the present review, is timely and justifiable. Macromer research is still in the beginning stage and many problems associated with preparations, properties and reactions of macromers are yet to be investigated.

References

1. R. Milkovich et al., U.S. Pat. 3,786, 116(1974).
2. T. Tsuruta et al., *ACS Polymer Preprint*, **20**, 539(1979), *Kobushi*, **28**, 192(1979).
3. S.F. Reed Jr., *Macromol. Syntheses*, **6**, 109(1976), C.A. Utaneck et al., *J. Polymer Sci.*, **46**, 535(1960).
4. A. Noshay and J.E. McGrath, "Block Copolymers," Academic Press, N.Y. 1977, p 39.
5. M.B. Berenbaum, "Encyclopedia of Polymer Sci. and Tech.," Vol. 11, 1969, p 425.
6. Poly (Ethylene Glycol) Dimethacrylates of Different Molecular Weights are Commercially Available from Ware Chemical Corp. Startfore, Conn. U.S.A.
7. D. M. French, *Rubber Chemistry and Technology*, **42(1)**, 71(1969).
8. Commercially Available from Jefferson Chemical Co. Houston, Texas, U.S.A.
9. G.M. LeFave et al., U.S. Pat. 3,278,496 (Oct. 11, 1966).
10. Phillips Petroleum Co., Brit. Pat. 945,851 (Jan. 8, 1964).
11. Phillips Petroleum Co., Brit. Pat. 944, 538 (Dec. 18, 1963).
12. D.J. Flory "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N.Y. 1953, p 31.
13. R.J. Ceresa, Ed., "Block and Graft Co-

polymerization," Vol. 2, John Wiley & Sons, N. Y. 1976, p 89.
14. M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience Pub., N. Y. 1968, p 85.
15. M. B. Berenbaum and R. H. Govran, West German Pat. 1,150,205(June 12, 1963).
16. C. H. Bamford et al., *Trans. Faraday Soc.*, **56**, 932(1960).
17. For examples; Y. Shimura and N. Ikeda, *J. Polymer Sci., Polym. Chem. Ed.*, **11**, 1271(1973), T. Shima et al., Jap. Pat. 70/12, 150(1970).
18. A. Noshay et al., *Ind. Eng. Chem., Prod Res. Dev.*, **12**, 268(1973).
19. T. W. Nakagawa and T. P. Rudy, U. S. Pat. 3,427,351(Feb. 11, 1969).
20. M. Brown and W. K. Witsiepe, *Rubber Age*, **104**, 35(1972).
21. I. Cho and K. W. Lee, *J. Korean Chem. Soc.*, **20**, 424(1976).
22. K. Okazaki et al., Jap. Pat. (69) 22, 535 and(69) 29,992(1969).
23. J. C. Galin, *Makromol. Chem.*, **124**, 118 (1969).
24. T. W. Brokks and C. L. Daffin, *ACS. Polymer Prepr*, **10(2)**, 1174(1969).
25. M. A. Novitskaya and A. A. Konkin, *Vysokomol. Soedin*, **7(10)**, 1719 (1965), *C. A.* **64**, 37106(1966).
26. G. Greber and A. Balciumas, *Makromol. Chem.*, **79**, 149(1964).
27. H. Tanka et al., Jap. Pat. (72)-29, 429 (1972).
28. P. Remp, "*Nato Advanced Study Institute Series on Reastions on Polymers*," D. Reidel Publishing Co. Dordsecht-Holland, 1973, p265.

—폴리머 기술뉴스—

殘油에서 에틸렌의 製造

Gulf Oil Chemicals社, Gulf Canada社 및 Stone & Webster Engineering社가 공동팀을 조성하여 燃料殘油를 含有하고 있는 原料에서 에틸렌를 製造하는 새로운 크랙킹法을 試驗하기 위하여 1,500萬달러의 파이롯트·플랜트를 建設하고 있다. 이 파이롯트·플랜트는 1980年에 가동할 것이다.

이 방법은 複熱크랙킹法(T. R. C)라고 부르며 從來法과 比較하여 많은 장점을 가지고 있다. 즉 設備가 經濟的이며 設備投資가 적고, 에너지 消費가 적다. 原料를 廣範圍하게 얻을 수 있으며 從來法으로는 사용할 수 없는 燃料 殘油等을 사용할 수 있다. 크랙킹을 정확하게 컨트롤할 수 있어 生成 에틸렌의 收率도 높다.

이같은 理由때문에 에틸렌製造 코스트를 約 20%節約할 수있다고 3社에서 말하고 있다.

(美, Chem, Week, Oct 24, 1979, p. 38)