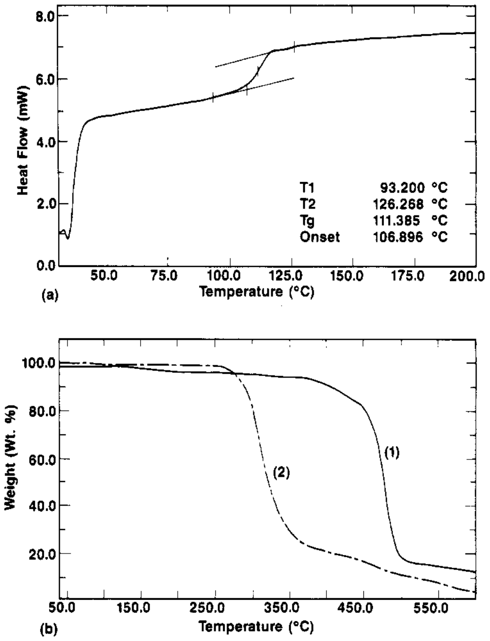

Figure 3. (a) DSC curve of poly(*exo*-5-hydroxynorbornene). (b) Curves 1 and 2 represent the TGA thermograms of poly(*exo*-5-hydroxynorbornene) and poly(vinyl alcohol), respectively.

The DSC curve of the polymer (Figure 3a) shows a glass transition temperature T_g at 111 °C. As expected, this is significantly higher than that of poly(norbornene). The TGA curve (Figure 3b) indicates that the polymer undergoes no significant weight loss up to a temperature of about 400 °C. This is in sharp contrast to poly(vinyl alcohol),[12] also a secondary alcohol, which begins to loose weight due to dehydration at a temperature as low as 260 °C (curve 2). The higher dehydration temperature of polymer III may be due to the presence of the OH group on the ring carbon that precludes the possibility of anti elimination. Another important reason could be the unfavorable introduction of ring strain upon dehydration. Furthermore the formation of a conjugated system in the case poly(vinyl alcohol) may cause its accelerated dehydration.

The growing interest in the area of metathesis polymerization and the development of new living metathesis catalyst systems makes the borane approach an attractive one for the synthesis of functional polymers with greater control over the final polymer structure. Further work toward the synthesis of polymers with other functional groups, such as NH_2, is currently under way.

Registry No. I, 121211-71-0; 9-BBN, 280-64-8; WCl_6, 13283-01-7; Me_4Sn, 594-27-4; 2,5-norbornadiene, 121-46-0.

References and Notes

(1) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Mol, J. C. CHEMTECH **1983**, 250. (c) Matsumoto, S.; Komatsu, K.; Igarashi, K. *Am. Chem. Soc., Symp. Ser.* **1977**, *59* 303. (d) Matsumoto, S.; Komatsu, K.; Igarashi, K. *Polymer Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1977**, *18*, 110.

(2) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

(3) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Krouse, S. A., Schrock, R. R. *Macromolecules* **1988**, *21*, 1885. (c) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 2640. (d) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640. (e) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1988**, *21*, 1961. (f) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

(4) However, there are a few exceptions such as WCl_6/Me_4Sn, which is known to be a robust catalyst that is tolerant to certain functional groups[1b] and yet can polymerize unstrained olefins such as cyclopentene.

(5) Brown, H. C. *Organic Synthesis via Borane*; Wiley-Interscience: New York, 1975.

(6) Chung, T. C. *Macromolecules* **1988**, *21*, 865.

(7) Ramakrishnan, S.; Berluche, E.; Chung, T. C., unpublished results.

(8) This very high selectivity has been observed and reported by Brown and co-workers, with hydroboration occurring by cis addition from the less hindered side of the double bond. Reference 3, page 343.

(9) Reference 1, page 260.

(10) For more experimental details check ref 5.

(11) A higher yield of 81% was obtained when the polymerization was carried out in the presence of an equimolar quantity of Et_3B.

(12) Pritchard, J. G. *Polyvinyl Alcohol, Basic Properties and Uses*: Gordon and Breach: New York, 1971.

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Anionic Polymerization of Fluorine-Containing Vinyl Monomers. 9. Hexafluoro-1,3-butadiene

Although tetrafluoroethylene is readily polymerized under free-radical conditions, numerous fluorinated vinyl monomers have not been polymerized with radical initiators. Ito et al. have reported methyl 2-(trifluoromethyl)acrylate (MTFMA) gives no polymer by the initiations with α,α'-azobis(isobutyronitrile) (AIBN), benzoyl peroxide, or γ-ray radiation.[1-3] Then 2-trifluoromethylacrylates have been readily polymerized by anionic polymerization technique because the e-value of MTFMA is very large.[4-6]

Fluorinated vinyl monomers possessing fluorine atoms at α-carbon of vinyl groups are more difficult to polymerize.[7] To obtain preliminary information on the general trend of the anionic polymerization of fluorinated butadienes, the present paper is concerned with the investigation of polymerization conditions of hexafluoro-1,3-butadiene (HFBD) by systematically surveying the typical anionic polymerization initiators and solvents. Radical polymerization of HFBD reported by Toy et al. has produced low molecular weight polymers,[8] and 1,4- and 1,2-addition reactions are found to take place with infrared spectrum of the polymer.

Anionic polymerization may thus be preferable to radical polymerization from the standpoint of production of poly(HFBD) possessing controlled microstructures.

Results of anionic polymerization of HFBD[9] (40 mmol) with cesium fluoride as initiator (0.8 mmol) in toluene or tetrahydrofuran (THF) (20 mL) are summarized in Table I. The polymerization system successfully produces high yields of poly(HFBD) both in toluene and THF. The polymers obtained are white solid material. This polymerization system is the first case that yields the appreciable amount of poly(HFBD) among the initiators examined in the series of this study. No polymer was obtained without cesium fluoride at 60 °C in toluene and THF.

The polymers obtained with cesium fluoride initiations are insoluble in any solvents such as hexane, cyclohexane, benzene, toluene, diethyl ether, THF, dioxane, methanol, ethyl acetate, acetone, chloroform, dichloromethane, pyridine, dimethyl sulfoxide, dimethylacetamide, hexamethylphosphoric triamide, *N,N,N′,N′*-tetramethylethylenediamine, 1,2- and 1,4-bis(trifluoromethyl)benzene,

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Table I
Polymerization of Hexafluoro-1,3-butadiene with Cesium Fluoride

initiator	solvent	temp, °C	time, days	yield, %
CsF	toluene	0	7	0
		20	7	20.8
		60	1	0
		60	7	58.9
		80	7	47.4
	THF	60	7	71.6

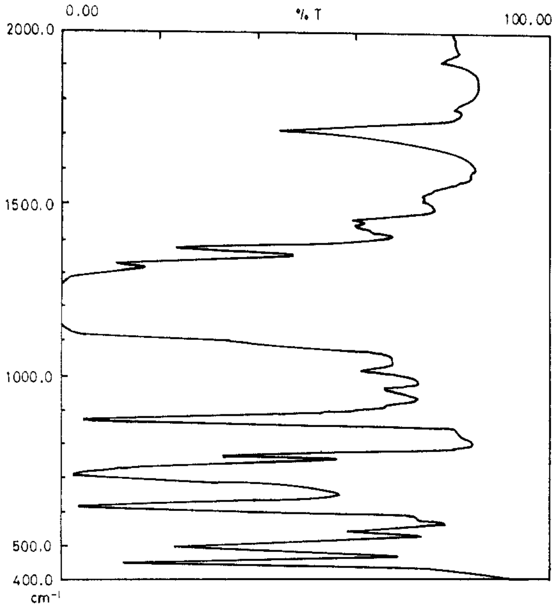

Figure 1. IR spectrum of poly(HFBD) obtained with cesium fluoride in toluene at 60 °C for 7 days (rolled film sample).

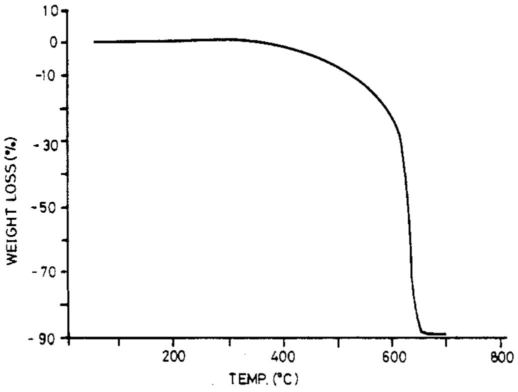

Figure 2. TGA of poly(HFBD) obtained with cesium fluoride in toluene at 60 °C for 7 days.

hexafluorobenzene, 2,2,2-trifluoro-1-(trifluoromethyl)ethanol, and 1,1,2-trichloro-1,2,2-trifluoroethane. The polymer is, therefore, precipitated as the polymerization reaction proceeds and the GPC eluogram is not recorded.

Figure 1 shows the infrared spectrum of poly(HFBD) obtained with cesium fluoride in toluene at 60 °C for 7 days.[11] The spectrum shows a very strong broad band between 1100 and 1300 cm^{-1} for C–F absorption. Toy et al. have reported that two characteristic absorption peaks at 5.6 μm (1786 cm^{-1}) and 5.8 μm (1724 cm^{-1}) are assignable to a pendant perfluorovinyl group and a CF=CF group, respectively.[9c] In Figure 1 a very small peak at 1775 cm^{-1} and a strong absorption at 1715 cm^{-1} are observable, which means the 1,4-moiety is suggested as the predominant configuration in the polymer.

The thermal character of polymer obtained was analyzed by thermogravimetric analysis (TGA). Figure 2 shows that poly(HFBD) is highly stable against heat, and the polymer begins to decompose at 360 °C.

Poly(HFBD) obtained here shows very high heat resistance though it possesses CF=CF groups in the polymer main chain. Various modifications and variations may be made by the reaction of this functional group with many reagents. This polymer is a new material having application in several fields and industries.

Further investigation on anionic polymerization of HFBD and characterization of poly(HFBD) obtained are in progress.

Registry No. HFBD (homopolymer), 25036-06-0; CsF, 13400-13-0.

References and Notes

(1) Ito, H.; Miller, D. C.; Wilson, C. G. *Macromolecules* **1982**, *15*, 915.
(2) Ito, H.; Giese, B.; Engelbrecht, R. *Macromolecules* **1984**, *17*, 2204.
(3) Iwatsuki, S.; Kondo, A.; Harashima, H. *Macromolecules* **1984**, *17*, 2473.
(4) Narita, T.; Hagiwara, T.; Hamana, H.; Nara, T. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 301.
(5) Narita, T.; Hagiwara, T.; Hamana, H.; Nara, T. *Polym. J.* **1988**, *20*, 277.
(6) Narita, T.; Hagiwara, T.; Hamana, H.; Maesaka, S. *Polym. J.* **1988**, *20*, 519.
(7) Wall, L. A., Ed. *Fluoropolymers*; Wiley-Interscience: New York, 1972.
(8) (a) Toy, M. S.; Lawson, D. D. *J. Polym. Sci., Part B* **1968**, *6*, 639. (b) Toy, M. S.; Newman, J. M. *J. Polym. Sci., A-1* **1969**, *7*, 2333. (c) Toy, M. S.; Stringham, R. S. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 717.
(9) HFBD was purified by passing through a calcium sulfate and molecular sieve column in vapor phase and collected at dry ice temperature under reduced pressure. Polymerization was carried out in a sealed glass ampule under purified nitrogen atmosphere. The reaction was terminated with hydrochloric acid/methanol and the reaction mixture was poured into methanol.[10] The solid polymer was filtered off and dried to constant weight.
(10) The initiators used here were prepared according to the following literature: (a) Narita, T.; Hagiwara, T.; Hamana, H. *Nippon Kagaku Kaishi* **1985**, 1945. (b) Narita, T.; Hagiwara, T.; Hamana, H.; Goto, M. *Makromol. Chem.* **1986**, *187*, 731. (c) Ishimori, M.; Hagiwara, T.; Tsuruta, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1165. (d) Kageyama, H.; Kasai, Y.; Suzuki, C.; Yoshino, N.; Tsuruta, T. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 89. (e) Narita, T.; Hagiwara, T.; Hamana, H.; Irie, H.; Sugiyama, H. *Polym. J.* **1987**, *19*, 985. (f) Narita, T.; Hagiwara, T.; Hamana, H.; Miyasaka, T.; Wakayama, A.; Hotta, T. *Makromol. Chem.* **1987**, *188*, 273.
(11) IR spectrum of a rolled film of poly(HFBD) was recorded. The authors would like to express their grateful acknowledgment to Prof. Masamichi Kobayashi at Osaka University for IR measurements.

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Photoinduced Release of Alkali Picrates Using Photoreactive Poly(crown ether)s

Crown ethers are well-known to dissolve alkali-metal salts into low polarity media by binding cations.[1] In this paper we report both the synthesis of polymers that have photochemically labile crown ether units and the pho-

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