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Asymmetric Reactions During the Polymerization of (*RS*)-Propylene Sulfide by *n*-Butyllithium–Lithium (−)-Menthoxide

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ABSTRACT: Studies of the polymerization of racemic propylene sulfide (PS) by *n*-BuLi-(−)LiOR* (* denotes chiral group) show that the development of optical activity in the polymers can arise both by the ordinary asymmetric selective polymerization of (*S*)-PS and by two secondary reactions: first, by selective desulfurization of (*R*)-PS (both the unreacted PS and the polymer have a negative rotation at small conversions of PS into polymer); and second, by selective decomposition of (*S*) polymer chains. The latter is also confirmed by the asymmetric decomposition of optically inactive poly(propylene sulfides) by the same catalytic system. Possible reaction mechanisms for these processes are considered.

The method of asymmetric synthesis of macromolecules has been widely used for solving fundamental questions in polymer chemistry. However, little attention has been paid to studies of the feasibility of finding asymmetric reactions involving both the monomer and the polymer chain which can occur in the course of the asymmetric synthesis of polymers. Recently it has been shown[1] that for the system *n*-BuLi-(−)LiOR* (LiOR*, lithium menthoxide) the asymmetric polymerization of (*RS*)-propylene sulfide (PS), involves three distinct mechanisms: (1) simultaneous PS desulfurization and PS polymerization with the formation of optically active polymers with the disulfide bonds; (2) decomposition of polymer chains with propylene evolution and the formation of oligomeric products; (3) oxidation of oligomeric products either by the elementary sulfur evolved or by lithium polysulfide with the formation of optically active polymers with much higher quantity of disulfide bonds.

Therefore it appears that the asymmetric stereoselectivity observed[1] is due to the participation of each of these three processes in asymmetric reactions. In the present paper we show the feasibility of bringing about both the asymmetric desulfurization of (*RS*)-PS and the asymmetric decomposition of the polymer, which takes place during polymerization of this monomer by the catalytic system *n*-BuLi-(−)LiOR*.

Experimental Section

All operations (purification of monomer and solvents, catalyst preparation, and polymerization) were carried out under dry argon. (*RS*)-Propylene sulfide (PS) (chromatographic purity 99.9%) was dried over calcium hydride and recondensed in the reaction vessels directly before use. *n*-BuLi-(−)LiOR* was prepared by reacting *n*-BuLi with *l*-menthol by the procedure described in a previous publication.[2] The organozinc catalysts were obtained from $ZnEt_2$ by a reported method.[1]

The PS desulfurization experiments were carried out in a special reaction system connected with a calibrated pressure gauge for determination of the conversion rate of PS into propylene. For the study of the optical properties of PS, the unreacted monomer was condensed out of the reaction ampoule into a vessel containing calcium hydride to remove the menthol. This operation was repeated many times until menthol was removed completely.

The polymers for the decomposition experiments were obtained by polymerization of PS with different anionic catalysts in sealed ampoules previously heated and degassed to 10^{-4} Torr. After the polymerization the reaction mixture was treated with dilute HCl and after three or four reprecipitations from benzene solution by methanol the polymer was dried under reduced pressure to constant weight.

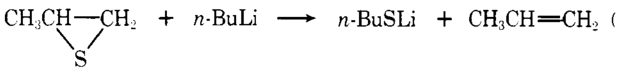
The decomposition of the polymers was carried out in sealed ampoules. The solvent (benzene) was added by vacuum transfer into vessels containing the necessary amounts of catalyst and polymer. Then catalyst solution was poured into the ampoule with the polymer solution. After decomposition the residual polymer was separated and purified as before.

All solvents used were purified according to procedures.[1,2]

The optical rotatory dispersions of the samples of monomers and polymers were measured with a Jasco ORD/UV-5 polarimeter, using 1.0-, 3.9-, and 10-cm cells.

Results and Discussion

Asymmetric Desulfurization of (*RS*)-PS. It is known that the formation of optically active polymers by the asymmetric selective polymerization of (*RS*)-PS with catalysts prepared from diethylzinc and asymmetric alcohols[3,4] occurs by the asymmetric selection of a preferred monomer antipode. However, in our case[1] the relatively high stereoselectivity of the process may be achieved in the stage of formation of the active centers for PS desulfurization, *i.e.*, in the stage preceding the process of polymerization.



$$CH_3CH(S)CH_2 + n\text{-BuLi} \longrightarrow n\text{-BuSLi} + CH_3CH{=}CH_2 \quad (1)$$

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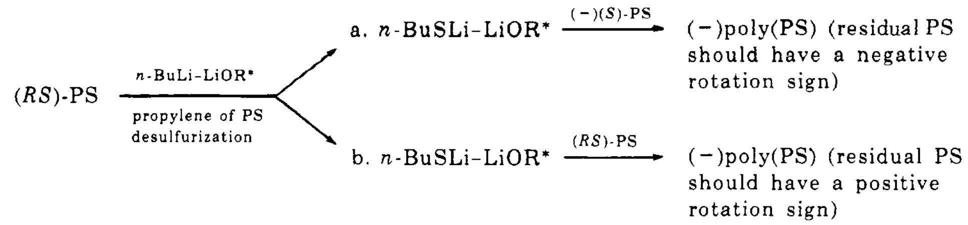
(1) A. D. Aliev, B. A. Krentsel, G. M. Mamediarov, I. P. Solomatina, and E. P. Tiurina, *Eur. Polym. J.*, 7, 1721 (1971).

(2) I. P. Solomatina, A. D. Aliev, and B. A. Krentsel, *Vysokomol. Soedin., Ser. A*, 11, 871 (1969).

(3) N. Spassky and P. Sigwalt, *C. R. Acad. Sci., Ser. C*, **265**, 624 (1967); *Eur. Polym. J.*, 7, 7 (1971).

(4) J. Furukawa, N. Kawabata, and A. Kato, *J. Polym. Sci., Part B*, **5**, 1073 (1967).

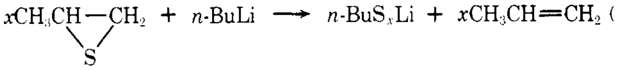
Scheme I



Two possibilities of desulfurization are conceivable: (a) the preferred (+)(*R*)-PS desulfurization and the usual nonasymmetric polymerization[5] of (−)(*S*)-enriched PS, since polymers with negative rotation are produced; and (b) the nonselective desulfurization of PS and the preferred polymerization of one of its antipodes, as usually observed in asymmetric stereoselective polymerization of racemic monomers (see Scheme I).

From this it is seen that from data on the optical rotation of the residual monomer at different degrees of conversion one can ascertain the true mechanism of asymmetric stereoselective PS polymerization.

The study of the kinetics of propylene evolution (Figure 1) in PS polymerization with this catalytic system shows that during the initial period (5 min) of the reaction there is intense evolution of propylene, the amount of which is approximately twice (1.73 times) that which should be formed[6] by reaction 1. After this point the rate of propylene evolution decreases but its evolution is not complete. The small conversion of PS into polymer even during a 10-15-min period (less than 15-25%) suggests (1) that the rate of PS desulfurization exceeds that of its polymerization and (2) that in addition to *n*-BuSLi, higher reactive lithium alkylpolythiolates *n*-BuS_xLi, which may also be active centers of PS polymerization, are also formed. The formation of *n*-BuS_xLi is also confirmed by the rapid appearance of the cherry-red color which is characteristic of the alkylpolythiolate anions[7] formed by the reaction



$$x\,CH_3CH{-}CH_2\ (\text{episulfide}) + n\text{-BuLi} \longrightarrow n\text{-BuS}_x\text{Li} + x\,CH_3CH{=}CH_2 \qquad (2)$$

(It is necessary to take account of the essential role of lithium alkoxide in all cases.) Indeed, the instantaneous appearance of this color is observed as well in the reaction of *n*-BuLi-LiOR* with elemental sulfur, during which alkylpolythiolates are probably produced by the reaction[7]

$$n\text{-BuLi} + S_8 \longrightarrow n\text{-BuS}_x\text{Li} + S_{8-x} \qquad (3)$$

It should be noted that the possibility of the reaction occuring by scheme (2) was not investigated earlier, as either equimolar or excess quantities of alkyl- (or aryl-) lithium were used in previous works to prevent the possible polymerization of episulfide compounds in the desulfurization reaction of episulfides.[8,9]

Studies of the optical rotatory dispersion (ORD) of the monomer 2.5 and 25 hr after the beginning of the reaction show (Figure 2) that it possesses appreciable optical activity with a negative sign in the visible region of the spectrum. The ORD curves are similar to those characteristic of (−)(*S*)-PS.[10] The sign of the rotations are $[\alpha]^{20}\text{D}$ −1.04 and −0.117° (neat) for the 2.5- and 25-hr samples. In the latter case, the polymer has a rotation of $[\alpha]^{20}\text{D}$ −27.6° in benzene.

Thus these data show that PS polymerization proceeds with selective desulfurization of (+)(*R*)-PS as well as the selective polymerization of (*S*)-PS. This may be due to the presence of centers of the type ∼S^-Li^+-LiOR*, which are less reactive than ∼$S_x^-Li^+$-LiOR*, there being a decrease of the rotation value of the monomer evolved in the course of polymerization.

Indeed, in a control PS polymerization with *n*-C_6H_{13}SLi-LiOR* polymer with a negative rotation ($[\alpha]^{20}\text{D}$ −31.2°, in benzene) and residual monomer with a positive rotation ($[\alpha]^{20}\text{D}$ +0.42°, neat) are produced; this is characteristic of the ordinary asymmetric selection polymerization of racemic monomers, in spite of a negligible PS desulfurization.

Thus, the course of this process with *n*-BuLi-LiOR* differs from those previously studied, where the configuration of the residual monomer was always opposite to that of monomer units in the polymer chain. This is due to the process of selective PS desulfurization. We believe that this is the first time that this has been demonstrated for episulfides.

Asymmetric Destruction of Poly(PS). It has been shown previously[1] that propylene evolution does not stop even after complete monomer conversion, but that the yield and the intrinsic viscosity of the polymer decrease as the polymerization time increases. This is probably associated with the cleavage of the polymer chains produced. Of particular interest is the problem of how the course of this reaction may affect the values of the optical rotation of the polymers produced. We have therefore studied the degradation of PS polymers produced by polymerization with symmetric catalysts.

It should be noted that Pino,[11] Tsuruta *et al.*,[12] and Furukawa *et al.*[13] have earlier shown that stereoregular polymers from racemic α-olefins and propylene oxide obtained by symmetric stereospecific catalysts can be separated into fractions with opposite signs of rotation by means of chromatography using optically active adsorbents. This is one of the methods of obtaining optically active polymers, while the separation itself convincingly shows that initial polymers are a racemic mixture of (*R*)- and (*S*)-enriched polymers.

Therefore, one could expect that in the decomposition of racemic poly((*RS*)-propylene sulfide) by the optically active reagent *n*-BuLi-LiOR*, there will be selective decomposition of (*R*) or (*S*) units. These reactions usually proceed at different rates because of the differences in activation energies of diastereoisomeric transition states. In fermentation reactions with racemic substrates these differences are known to be considerable and because of this reactions often proceed with complete stereospecificity.

(5) N. Spassky and P. Sigwalt, *Tetrahedron Lett.*, 32, 3541 (1968).
(6) B. M. Trost and S. Ziman, *Chem. Commun.*, 5, 181 (1969).
(7) B. D. Vineyard, *J. Org. Chem.*, 32, 3833 (1967).
(8) R. Cammereck, C. J. Fettes, and M. Morton, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 11, 72 (1970).
(9) N. P. Neureiter and F. G. Bordwell, *J. Org. Chem.*, 24, 578 (1959).
(10) I. P. Solomatina, Thesis, Moscow, 1971.
(11) P. Pino, *Chim. Technol. Polym.*, 12, 54 (1967).
(12) T. Tsuruta, S. Inoue, and I. Tsukuma, *Makromol. Chem.*, 84, 298 (1965).
(13) J. Furukawa, S. Akutsu, and T. Saegusa, *Makromol. Chem.*, 94, 68 (1966).

Table I
Decomposition of Poly((*RS*)-propylene sulfide) by *n*-BuLi-LiOR* [a]

	Initial Poly(propylene sulfide)					Obtained Poly(propylene sulfide)				
No.	Obtained by	$[\alpha]^{20}{}_{D}$ [c] (deg)	$[\eta]^{25}$ C_6H_6 (dl/g)	$M \cdot 10^{-4}$ [d]	Time of Dec (Days)	% Yield	$[\eta]^{25}$ C_6H_6 (dl/g)	$M \times 10^{-4}$ [d]	$[\alpha]^{20}{}_{D}$ [c] (deg)	$[\alpha]^{20}{}_{400}$ [c] (deg)
1	$CdCO_3$ in H_2O	0	1.26	21.2	30	30.6	0.045	0.44	0.70	1.74
2	*n*-BuLi	0	0.44	6.2	20	37.1	0.073	0.77	1.01	2.50
3	$ZnC_2H_5(OCH_3)$	0	0.74	11.1	16	64.3	0.095	1.05	0.36	0.93
4[b]	$Cd(SCH_2CH{=}CH_2)_2$	0	0.36	4.9	0.75	59.6	0.098	1.07	0.17	0.43
5[b]	$Cd(SCH_2CH{=}CH_2)_2$	0	0.36	4.9	4	35.0	0.063	0.65	2.84	15.70
6	$Zn(C_2H_5)_2$-2R*OH	18.6	0.95	12.8	27	86.6	0.60	5.89	14.6	44.10
7	$Zn(C_2H_5)_2$-2R*OH	29.4	0.98	13.4	60	64.0	0.405	4.02	12.1	37.70

[a] Temperature 25°; molar ratio (calculating per one monomer unit) of poly(PS)-*n*-BuLi = 20; benzene, 15 ml; poly(PS) 0.6-1.0 g. [b] Poly(PS)-*n*-BuLi = 5. [c] Measured at l = 0.39 dm, c = 3 g/100 ml, benzene. [d] Molecular weight was estimated from the relation (V. E. Eskin and A. E. Nesterov, *Vysokomol. Soedin., Ser. A*, 8, 141 (1966)): $[\eta]^{25} = 0.33 \times 10^{-4} M^{0.86}$.

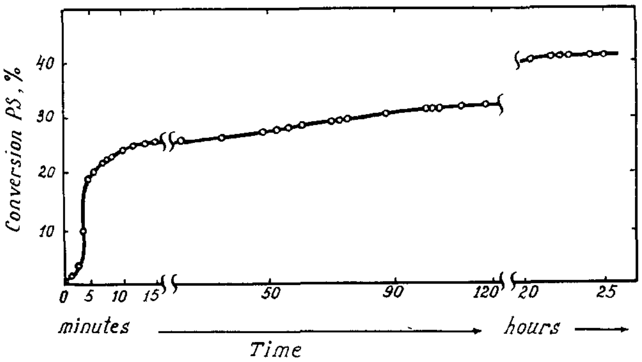


Figure 1. The conversion of PS to proplylene during the PS bulk polymerization initiated by *n*-BuLi-LiOR* (molar ratio PS-BuLi = 10, temperature 25°).

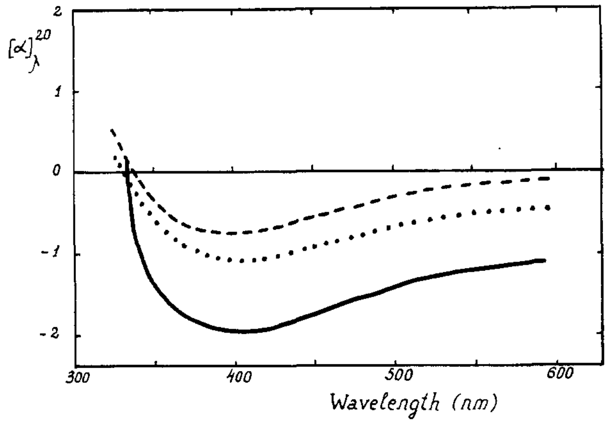
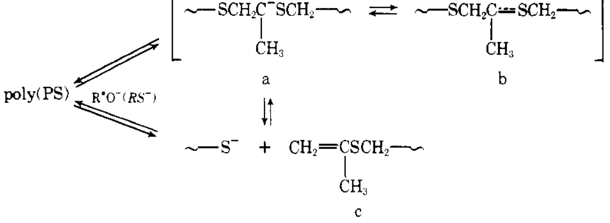


Figure 2. ORD curves of unreacted PS (the experimental conditions for the polymerizations are the same as Figure 1): dashed line, after 25 hr; solid line, after 2.5 hr; dotted line, (−)PS evolved during PS polymerization by the system $ZnEt_2$-(+)-β-phenylalanine (poly(PS) having a positive rotation sign).

Table I shows that, independent of the conditions of producing the initial poly(PS) samples, during their asymmetric destruction relatively low molecular weight optically active polymers are formed, the rotation sign of which is opposite to that of the catalyst. This shows that (1) the optical activity obtained cannot be attributed to (−)-menthoxy groups since similar compounds of (−)-menthol have a negative rotation sign, and that (2) polymer chains or sequences of monomer units having the (*S*) configuration of asymmetric carbon atoms are subjected to selective decomposition.

It should be noted that the data obtained do not permit conclusions about the peculiarity of the asymmetric cleavage mechanism of racemic poly(PS), since the initial samples differed both in stereoregularity and, because of the difference of their molecular weights, in the contents of -SH end groups reacting with *n*-BuLi. However, these data suggest that, unlike the method of chromatographic separation, kinetic methods of destruction do not require the use of stereoregular crystalline macromolecules to obtain optically active polymers. Thus, the data obtained show that in asymmetric PS polymerization by *n*-BuLi-LiOR* the selective desulfurization of (+)(*R*)-PS, and the preferred polymerization of (−)(*S*)-PS (reactions increasing optical yields of polymers) occur at active centers of the type ⁓S^-Li^+-LiOR* with the formation of (−)poly(PS). However, the decomposition rate of the latter is higher than that of (+)poly(PS), which results in a decrease of the optical yield of polymers (Table I).

Table I shows that the reaction of (+)poly(PS) decomposition by the same catalyst proceeds at a lower rate. However, the observed decrease in optical activity of the polymers evolved was surprising. This was not because of selective decomposition of monomer units with (*R*) configuration of asymmetric carbon atoms but was apparently due to the following causes. (1) The occurrence of an equilibrium of the type



which results in racemization. Unlike ethers the decomposition rate of which is higher despite their lower CH acidity in comparison with respective thioethers[14] the 3d-orbital effect of type b decreases the probability of decomposition of polymers at stage a. Even if the decomposition proceeds *via* α or β elimination of a proton, the high reactivity of vinylthioethers with mercaptans (especially mercaptans with a sulfur atom in β position with respect to SH groups[15]) in the presence of basic compounds, also contributes to equilibrium of the type (poly(PS) ↔ a ↔ b ↔ c) and hence to racemization.

(2) The formation of end groups of two types having a

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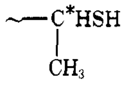
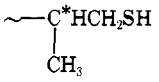
(14) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, **20**, 417, 427 (1964).
(15) E. E. Reid, "Organic Chemistry of Bivalent Sulphur," Vol. 2, Chemical Publishing Co., Inc., New York, N. Y., 1960.

different contribution to the optical rotation


$\sim\!\!-\underset{\mathrm{CH_3}}{\mathrm{C^*}}\mathrm{HSH}$

d


$\sim\!\!-\underset{\mathrm{CH_3}}{\mathrm{C^*}}\mathrm{HCH_2SH}$

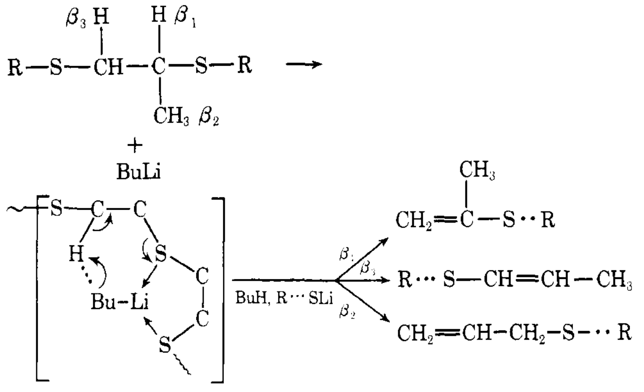
e

Since during the decomposition of the polymer the quantity of SH groups increases and more low molecular polymers are produced, one should take into account the differences of contributions to the rotation of these groups d and e. If they are compared with the corresponding model compounds,[16] then for the type d, (+)(*S*)-2-butanethiol and (+)(*S*)-1-methylpropylethylthioether have $[\alpha]^{20}\mathrm{D}$ 34.4 and 31.6°, respectively, while for the type e, (+)(*S*)-2-methylbutanethiol and (+)(*S*)-2-methylbutylethylthioether have $[\alpha]^{20}\mathrm{D}$ 3.57 and 20.67°, respectively, *i.e.*, one can see a great difference in the values of rotation between mercaptan and thioether in structures of type e.

Unfortunately, preliminary experiments on carrying out the reaction of SH groups with CH_3I, the result of which might be some increase of rotation, have been unsuccessful because of the formation of by-products, particularly polysulfonium compounds.

On the basis of the results obtained one may propose that during decomposition of the polymer chains by *n*-BuLi-LiOR* reaction occurs by the following scheme.

(1) Decomposition by n-BuLi by the mechanism of β elimination *via* the following transition states (type A)[17]



A

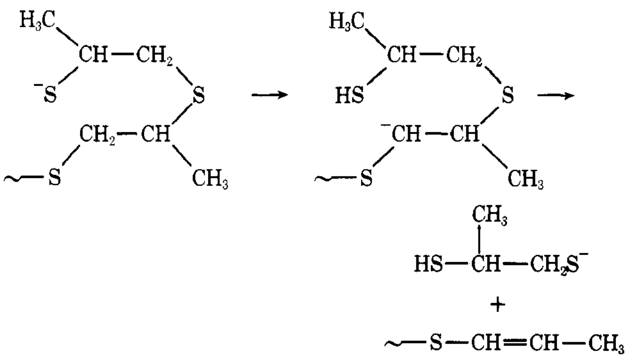
However, by this scheme for the decomposition of one C-S-C bond an equimolar quantity of *n*-BuLi is necessary, which does not explain the further decomposition. Indeed, during PS polymerization *n*-BuLi is almost quantitatively used up in the initial period by PS desulfurization and since the decomposition takes place even after desulfurization, this shows that the fragments of RSLi-LiOR* are still reactive.

(2) For intramolecular (or intermolecular) decomposition, see Scheme II.

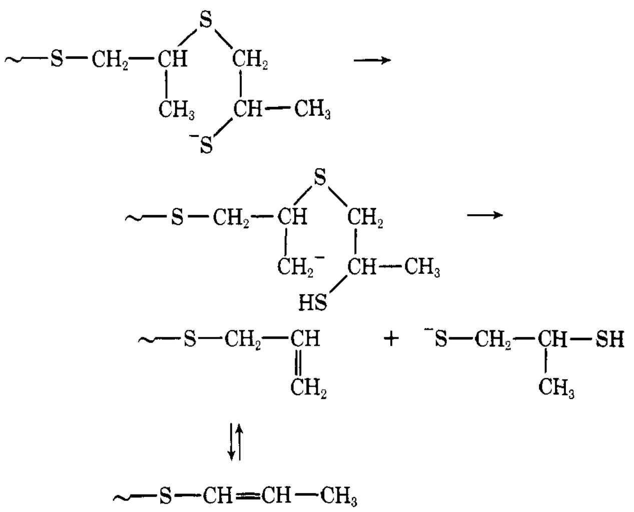
In both types of decomposition by β-elimination allyl sulfides are formed which are readily isomerized to vinyl sulfides. In the second case, the β elimination occurs by thiolate anions, which is quite probable, especially for β_1 and β_3 elimination, since hydrogen atoms which are adjacent to a sulfur atom are the most "acidic" and the stabilization of the carbanion formed by the vacant 3d orbital of the sulfur atom is feasible.[18] In addition, the role of alkoxide anion in increasing the total basicity and nucleophilicity of a medium is well known.[19] It should be noted that in polymer separation (after decomposition reactions) in a slightly acidified medium the cleavage of S-C=C bonds occurs with the formation of SH end groups.

Scheme II

β_3 (and β_1) elimination

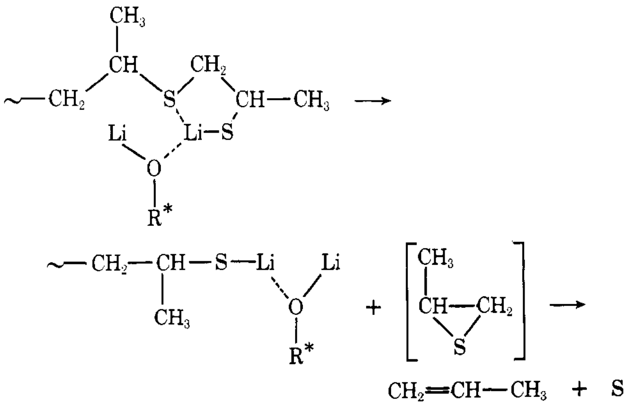


β_2 elimination



The occurrence of both of these decomposition reactions does not, however, explain the formation of propylene.

(3) Decomposition by the depolymerization mechanism



This type of decomposition of polythioether is similar to that of polyethers, the destruction of which (polyaldehydes, etc.) is accompanied by the evolution of a monomer.[20] In addition, poly(PS) having SH end groups is known to be highly unstable and during storing decomposes considerably.

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(16) P. Salvadori, L. Lardicci, and M. Stagi, *Gazz. Chim. Ital.*, 98, 1400 (1968).

(17) E. J. Vandenberg, *Intern. Symp. Macromol. Chem., Tokyo-Kyoto,* 1966, Prepr. 5.5.02.

(18) W. Tagaki, T. Tada, R. Nomura, and S. Oae, *Bull. Chem. Soc. Jap.*, 41, 1696 (1968).

(19) J. F. Bennett and E. Bacciochi, *J. Org. Chem.*, 32, 11 (1967).

(20) V. V. Korshak and S. V. Vinogradova, *Usp. Khim.*, 37, 2066 (1968).

Elementary sulfur, evolved during the decomposition of polymer chains by the depolymerization mechanism, contributes to the rapid formation of alkylpolythiolate anions which are reactive during the decomposition reaction and may take part in the formation of disulfide bonds in polymers. Experimentally a negligible increase of elemental sulfur was observed in decomposed polymer samples.

It should be noted here that in the asymmetric decomposition of other polymers, in particular that of poly(propylene oxide), optically active products are also formed.[10]

Taking into consideration the relative facility of the cleavage of polyether in comparison with polythioethers and the fact that, using the catalytic system $ZnEt_2$-$2R^*OH$, asymmetric cleavage of the polymer chains obtained also takes place but to a lesser extent,[10] one can suppose that upon separation of racemic poly(propylene oxide) by the optical active absorbents $ZnEt_2$-(−)R^*OH or (+)-borneol, asymmetric destruction of polymer occurred. Because of the absence of data on the molecular weights of initial and fractionated polymers,[13] a supposition can be made that these absorbents react more rapidly with the *l*- (or *d*-) polymer chains, decomposing them to polymers with R^*O-Zn-O-··· end groups, which, unlike the free *d*- (or *l*-) polymer chains, are not eluated by *n*-heptane. In our case, when the optically inactive poly(PS) ($[\eta]^{25}$ 1.1 dl/g) was kept for 145 hr in the presence of $ZnEt_2$-$2R^*OH$, an optically active polymer with $[\alpha]^{20}{}_D$ 8.75° and $[\eta]^{25}$ 0.9 dl/g was obtained.

Thus the asymmetric destruction of racemic macromolecules provides new possibilities for the synthesis of optically active polymers and, in addition, it affords low molecular compounds with known optical activity, which is very important for the determination of the efficiency of asymmetric cleavage and the stereospecificity of optically active reagents.

These two processes, selective desulfurization and selective decomposition, are useful additions to the classical methods of separation of racemic compounds used in developing asymmetric syntheses.

Structure and Reactivity in Cationic Polymerization of 2-Alkoxybutadienes

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ABSTRACT: The structure and reactivity in cationic polymerization of 2-alkoxybutadienes were studied. The butadienes used are methoxy-, ethoxy-, isopropoxy-, *tert*-butoxy-, and 2-chloroethoxybutadienes (MOBD, EOBD, IPOBD, tBOBD, and CEOBD, respectively). The four butadienes, except for tBOBD, had a coplanar structure as to diene and *O*-alkyl bond, and the charge on carbon 1 was large. EOBD polymerized fairly rapidly at 0° with several cationic catalysts. The principal products were methanol-soluble oligomer and methanol-insoluble polymer, both of which had 1,4 structure. The relative reactivities of these butadienes were determined from the copolymerizations with ethyl vinyl ether as follows: IPOBD > EOBD > CEOBD > MOBD (>tBOBD).

There have been many investigations on the structure-reactivity relationship in cationic polymerization of alkyl vinyl ethers.[1] One of the characteristics of alkyl vinyl ethers is particularly large reactivity in cationic polymerization owing to the presence of an oxygen adjacent to the vinyl group. On the other hand, many cationic polymerizations of linear conjugated dienes also have been investigated—the cationic polymerizations of butadiene,[2] 2,4-hexadienes,[3] 1- and 2-phenylbutadienes,[4] 1-ethoxybutadiene,[5] and so on. The polymers obtained from these dienes, however, often possess small molecular weights and complex structures.

2-Alkoxybutadiene is regarded as an alkyl vinyl ether as well as a butadiene derivative. For the former case, the α-vinyl group is a substituent; for the latter case, the 2-alkoxy group is a substituent. The importance of each substituent is dependent on the nature of a reaction. Studies on the effect of substituent in such a compound may, therefore, shed light on the nature of a reaction. For instance, Fedor *et al.* have investigated whether 4-methoxy-3-buten-2-one and several 3-alkoxycrotonates are hydrolyzed as a vinyl ether or as a vinyl ketone.[6]

The lone-pair electrons of oxygen in a vinyl ether migrate to the double bond, which makes a vinyl ether basic and reactive in electrophilic reactions. It is interesting to know how this effect is manifested in the molecular properties and cationic polymerizability of 2-alkoxybutadienes. Probably, the coplanarity between diene and an alkoxyl group is affected by increasing the bulkiness of the alkyl group. It is not known how reactive a 2-alkoxybutadiene is in cationic polymerization or whether it produces a high polymer.

In this paper, the molecular structure, properties, cationic polymerizability, and polymer microstructure of several 2-alkoxybutadienes are studied. The results are discussed in comparison with those of alkyl vinyl ethers.

Experimental Section

Materials. Five 2-alkoxybutadienes, that is, 2-methoxybutadiene (MOBD), 2-ethoxybutadiene (EOBD), 2-isopropoxybutadiene (IPOBD), 2-*tert*-butoxybutadiene (tBOBD), and 2-(2-chloroethoxy)butadiene (CEOBD), were prepared by Petrow's method[7]

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(1) See, for example, (a) T. Higashimura, J. Masamoto, and S. Okamura, *Kobunshi Kagaku*, **26**, 702 (1968); (b) H. Yuki, K. Hatada, and M. Takeshita, *J. Polym. Sci., Part A-1*, **7**, 667 (1969); (c) T. Higashimura, T. Masuda, S. Okamura, and T. Yonezawa, *J. Polym. Sci., Part A-1*, **7**, 3129 (1969).

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