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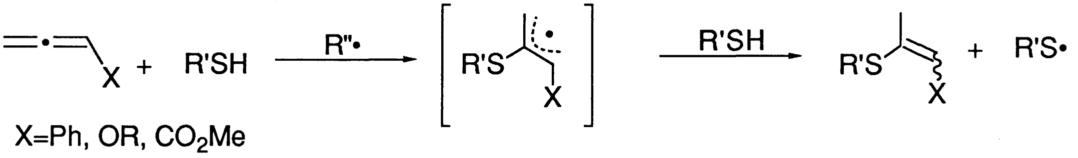
Radical Polyaddition of Dithiols to 1,4 -Bis(allenyloxy)xylylene. Synthesis of Functional Polymer Containing Reactive Carbon-Carbon Double Bonds in the Backbone

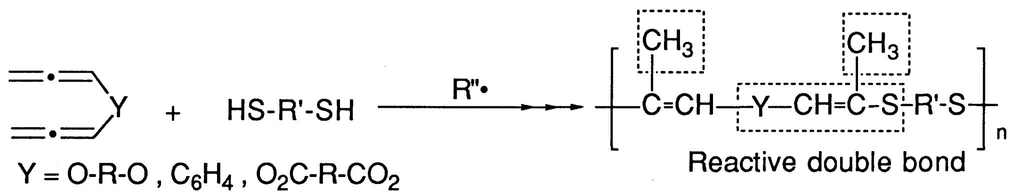
Tsutomu YOKOZAWA, Eiichi SATO, and Takeshi ENDO*
Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

Radical polyadditions of 1,4-benzenedithiol or bis(4-mercaptophenyl)sulfide to 1,4-bis(allenyloxy)xylylene were described. Thiol groups added to the terminal double bonds of allenyloxy groups selectively to give polymers containing both reactive carbon-carbon double bonds in the main chain and methyl groups in the side chain. The obtained polymers easily underwent crosslinking by the reaction of the double bonds in the backbone with Lewis acid.

Allene derivatives are expected to be very attractive as one of reactive vinyl monomers containing a cumulated carbon-carbon double bond, and can be converted into functional polymers having *exo*-methylene groups by the selective polymerization of one of the two double bonds in allenes. In our investigation on the polymerization of allene derivatives,[1)] we have already reported selective radical additions of thiols to alkoxyallenes,[2a)] phenylallene,[2b)] and carbomethoxyallene[2c)] as model reactions of the radical polymerizations; this reactions proceed only by the terminal double bond of allenes in all cases (Eq. 1), despite non-selective radical additions of thiols to unsubstituted allene[3)] and alkylallenes.[4)] It occurred to us that an attractive other route to polymerization of allene derivatives would be opened if diallenes containing the skeletons of alkoxyallene, phenylallene, and allenic ester could be allowed to react with dithiols in the presence of radical initiators. These resulting polymers will be also expected to serve as functional polymers containing various kinds of reactive carbon-carbon double bonds, and high solubility of the polymers based on methyl groups in the side chain is also anticipated (Eq. 2), contrary to insoluble unsaturated polymers obtained by the radical polyaddition of dithiols to diynes.[5)]



(1)



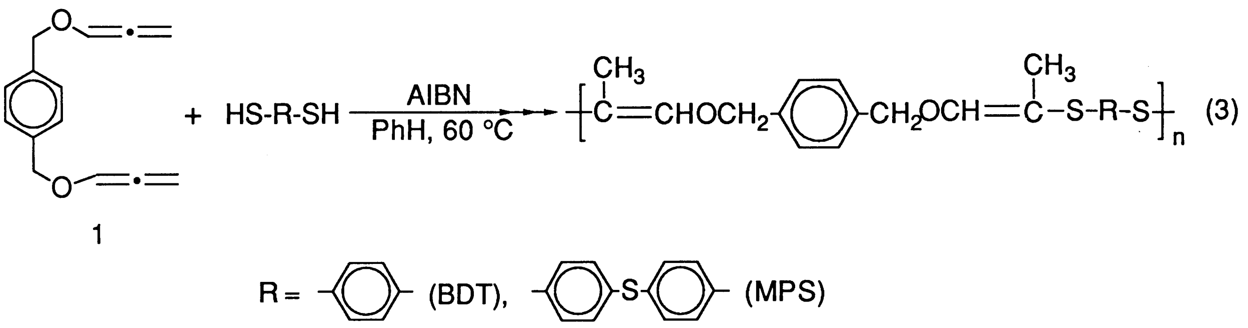
(2)

Herein we wish to report the polyadditions of aromatic dithiols to 1,4-bis(allenyloxy)xylylene (**1**), which afford high molecular weight polymers containing reactive electron-rich double bonds substituted by oxygen and sulfur atoms; these polymers can be easily converted into crosslinked polymers by Lewis acid.

The requisite diallene **1** was prepared by isomerization of the corresponding propargyl ether, 1,4-bis(propargyloxy)xylylene6) in the presence of a catalytic amount of potassium *tert* -butoxide7) according to the method for monofunctional alkoxyallenes.8) The polyadditions of aromatic dithiols9) such as 1,4-benzenedithiol (BDT) or bis(4-mercaptophenyl)sulfide (MPS) to **1** were carried out at 60 °C in benzene in the presence of azobis(isobutyronitrile) (AIBN) as a radical initiator. The polymers obtained were purified by reprecipitation in hexane. The results are summarized in Table 1. In both polyadditions of BDT and MPS to **1**, polymer yields are almost quantitative irrespective of reaction time, whereas their average molecular weights increase with time, indicating that the polymerization proceeds via polyaddition without serious side reactions.

All of polymers obtained here were soluble in benzene, dichloromethane, chloroform, tetrahydrofuran, etc., as expected by us. The IR spectra of the polymers showed the characteristic absorptions of a trisubstituted carbon-carbon double bond at 1641-1640 and 814-811 cm^{-1}, and an absorption attributable to a vinyl ether group at 1263 cm^{-1}. The ^{1}H NMR spectra measured in C_6D_6 showed signals corresponding to the olefinic protons at 6.60-6.58 and 6.13-6.12 ppm, and signals assignable to the methyl protons attached to an olefinic carbon at 2.05-2.01 and 1.72-1.71 ppm with the ratio 1 : 3. These spectral data indicate that the resulting polymers consist of one unit formed by addition of the thiol group of BDT or MPS to only the terminal double bond of **1** (Eq. 3).

Newly formed carbon-carbon double bonds in the polymers contained both *E* and *Z* structure, the ratio of which was estimated by ^{1}H NMR using the ratio of signal areas for the two different types of methyl protons.10) The assignment of stereochemistry has been made on the basis that in the carbon-carbon double bond assigned as *Z* the methyl and olefinic protons appear at lower field in the NMR. The ^{1}H NMR spectrum of the model compound, obtained by the radical addition of thiophenol to allenyl benzyl ether,11) showed similarity of that of the polymers, and strong correlation in 500 MHz ^{1}H NOESY NMR spectrum was observed between the methyl protons at lower field and the olefinic proton at lower field, indicating the signals for *Z* isomer. The *E*/*Z* ratio of the double bonds in the polymer obtained from both BDT and MPS was changed from ca. 1/1 to 1/9 with reaction time, and similar tendency was also observed in the model reaction of allenyl benzyl ether with thiophenol.11,12)



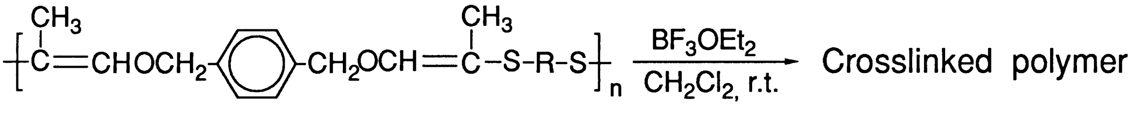
(3)

Table 1. Radical polyaddition of dithiols to **1** [a)]

Dithiol	Time/h	Yield/%	$\overline{M}$n [b)]	*E*/*Z* [c)]
BDT	3	95	2700	48/52
BDT	6	98	5500	27/73
BDT	12	90	6000	14/86
BDT	24	95	8000	12/88
BDT	48	96	9600	12/88
MPS	3	92	3800	47/53
MPS	6	98	4000	39/61
MPS	12	92	5900	35/65
MPS	24	88	9600	14/86
MPS	48	97	11500	12/88

a) An equimolar of **1** and dithiol polymerized at 60 °C with AIBN in benzene (2.5 mol/L).
b) Estimated by GPC based on polystyrene standard. c) Estimated by ^{1}H NMR.

Furthermore, crosslinking of the polymer was carried out with BF_3OEt_2 by utilizing the reactive electron-rich carbon-carbon double bonds in the backbone. To a solution of the polymer in dichloromethane was added 3 mol% of BF_3OEt_2 at room temperature to give a crosslinked polymer quantitatively in 30 sec (Eq. 4). Since characteristic absorptions of a double bond in the polymer at 1640 and 814 cm^{-1} disappeared almost completely in the IR spectrum of the resulting crosslinked polymer, the reactive electron-rich double bonds in the backbone of different polymer chain may undergo cationic polymerization to afford the crosslinked polymer.



(4)

In summary, the present work has demonstrated that functional group-substituted diallene such as **1** can be utilized for selective radical polyaddition of dithiols. Furthermore, the obtained polymers have high solubility in common organic solvents and contain reactive electron-rich double bonds, by which crosslinking can take place with Lewis acid and other functions will be able to be introduced. Further works on the polyadditions of dithiols to other diallenes as well as applications of the resulting polymers as functional materials are in progress.

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References

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6) 1,4-Bis(propargyloxy)xylylene was prepared by etherification of propargyl alcohol with xylylene dichloride in the presence of sodium hydroxide and a catalytic amount of tetrabutylammonium bromide in 88% yield. IR (neat) 2118, 1083 cm^{-1}; ^{1}H NMR (CCl_4, TMS) δ 7.24 (s, 4H), 4.52 (s, 4H), 4.08 (d, J = 2.4 Hz, 4H), 2.30 (t, J = 2.4 Hz, 2H).

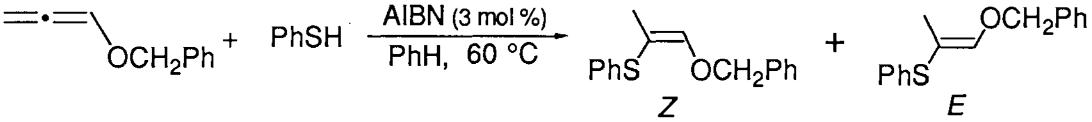
7) Diallene **1** was purified by column chromatography on silica gel (hexane). Yield 58%; IR (neat) 1954, 1197cm^{-1}; ^{1}H NMR (CCl_4, TMS) δ 7.24 (s, 4H), 6.84 (t, J = 6.0 Hz, 2H), 5.29 (d, J = 6.0 Hz), 4.55 (S, 4H). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.52; H, 6.59. Found: C, 77.98; H, 6.60.

8) S. Hoff, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **87**, 916 (1968).

9) In the case of aliphatic dithiols, the formation of a crosslinked polymer was mainly observed.

10) The determined *E*/*Z* ratios were in good agreement with that calculated from two different types of olefinic protons (6.60-6.58 and 6.13-6.12 ppm) in ^{1}H NMR and of methyl carbons (18.9 and 15.8 ppm) in ^{13}C NMR.

11) The reaction of allenyl benzyl ether with an equimolar thiophenol was carried out at 60 °C in the presence of AIBN in benzene to give a trisubstituted olefin which was formed by addition of thiol to the terminal double bond of allene (*E*/*Z* = 10/90). Column chromatography on silica gel (hexane) afforded pure *Z* isomer, NOESY spectrum of which was taken. ^{1}H NMR (C_6D_6, TMS) δ 7.53-7.07 (m, 10H), 6.60 for *Z* isomer and 6.37 for *E* isomer (2t, J = 1.6 Hz, 1H), 4.90 (s, 2H), 1.90 for *Z* isomer and 1.73 for *E* isomer (2d, J = 1.6 Hz, 3H).



12) Pasto *et al.* has also reported that *Z* isomer is predominantly formed in the reaction of methoxyallene with thiophenol, and that there is thermodynamic equibration of both isomers in the reaction and *Z* isomer is lower in energy from the results of ab initio MO calculations on models for *E* and *Z* isomer.[2d)]

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