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Cationic Polyaddition of *p*-Xylylene Glycol to 1,4-Bis(allenyloxy)xylene. Synthesis of Functional Polyacetal Containing Vinyl Groups in the Side Chain

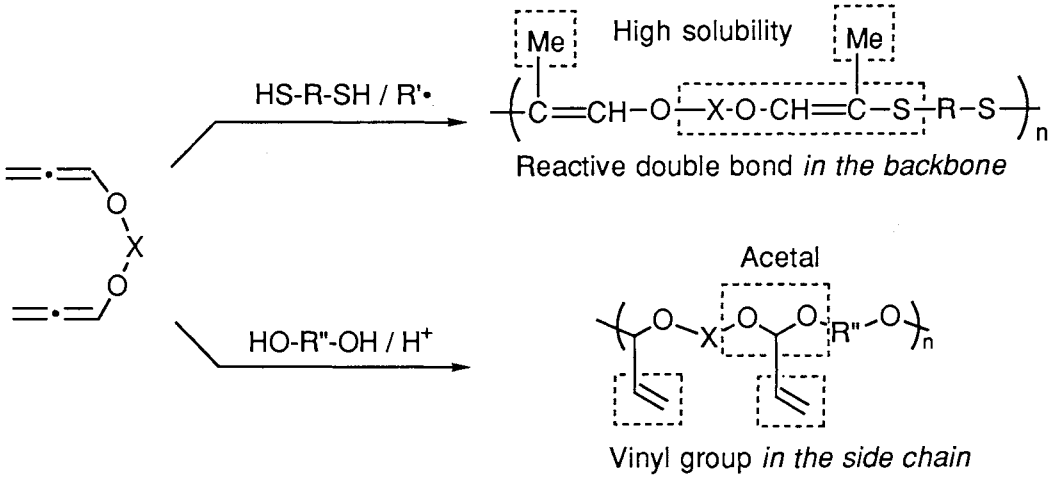
Eiichi SATO, Tsutomu YOKOZAWA,† and Takeshi ENDO*

Research Laboratory of Resources Utilization,

Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

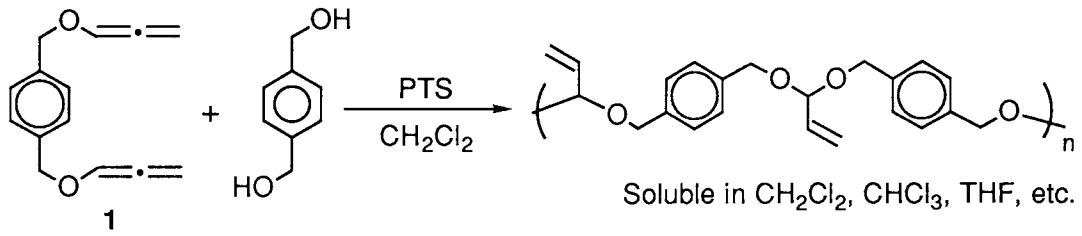
Polyaddition of *p*-xylylene glycol to 1,4-bis(allenyloxy)xylene was examined. Hydroxy groups of the diol added to the internal double bonds of allenyloxy moieties of bis(alkoxyallene) selectively to afford polymers containing both vinyl groups in the side chain and acetal skeleton in the main chain. The obtained polymer was degradable by the reaction of acetal skeleton in the backbone with aqueous acid.

Recent work has centered on the polymerization of allene derivatives for the synthesis of new functional polymers containing carbon-carbon double bonds.[1] We have recently reported the radical polyaddition of dithiols to bis(alkoxyallene), 1,4-bis(allenyloxy)xylene (**1**), which affords functional polysulfides containing carbon-carbon double bonds *in the backbone* by the addition of thiols to the *2,3-double bond* of the allene.[2]



† Present address: Department of Applied Chemistry, Kanagawa University, Rokkakubasi, Kanagawa-ku, Yokohama 221.

Hoff's report[3] of selective addition of alcohols to the *1,2-double bond* of alkoxyallenes in the presence of an acid catalyst suggested that the reaction of diol with bis(alkoxyallene) may permit us to synthesize a new allene polymer containing carbon-carbon double bonds *in the side chain.* We wish to report the acid-catalyzed polyaddition of diol to **1**, which affords a polyacetal with vinyl groups in the side chain.



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The polyadditions of a diol such as *p*-xylylene glycol to **1** were carried out in CH_2Cl_2 with a catalytic amount of *p*-toluenesulfonic acid (PTS) or pyridinium *p*-toluenesulfonate (PPTS). The obtained polymers were purified by reprecipitation in methanol or high pressure liquid chlomatography. The results are summarized in Table 1. When the reaction was carried out in the presence of PTS at -10 °C, structually complicated polymer and cross-linked polymer were obtained. Thus, the reaction temperature was decreased to -30 °C to obtain only soluble polymers as expected. The polymer yield and molecular weight increased with time in the presence of PTS (1 mol%), whereas the molecular weight did not increase with the amount of PTS. When PPTS was used instead of PTS, the polymerization did not proceed at -30 °C, and even at -10 °C only low molecular weight polymer was obtained.

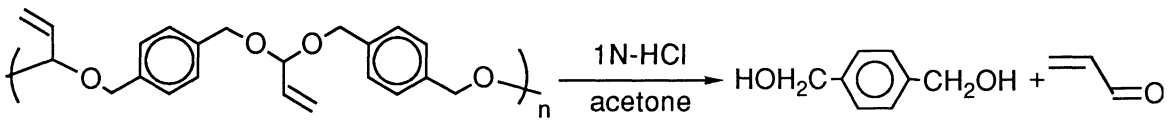
The IR spectra of the soluble polymer showed the characteristic absorptions ascribed to a vinyl group at 1643, 937 cm^{-1}. The ^1H NMR and ^{13}C NMR spectra measured in CDCl3 showed the multiplet signals corresponding to the vinyl protons at 6.23-4.90 ppm and the signal based on the acetal carbon at 100.24 ppm, respectively. Furthermore, these spectra of the polymer showed a complete similarity to the spectrum of a model compound which was prepared by addition of benzyl alcohol to benzyloxyallene.[4] These spectral data supported that the resulting polymers consisted of one unit formed by addition of the hydroxy group of glycol to only the 1,2-double bond of **1**.

Table 1. Cationic polyaddition of diol to **1**[a)]

Catalyst (mol%)	Temp / °C	Time / h	Yield / %[b)]	$\overline{Mn}$[c)]
PTS (0.25)[d)]	-10	2	58[e)](12)[f)]	27500
PTS (1)	-30	2	52	3200
PTS (1)	-30	3	64	8900
PTS (1)	-30	6	81	9300
PTS (5)	-30	3	69[g)]	2300
PTS (10)	-30	3	71[g)]	3000
PPTS (1)[d)]	-30	6	0	
PPTS (1)	-10	72	51[g)]	1600

a) The polyaddition was carried out in CH_2Cl_2 (0.2 mol/L) under Ar atmosphere. b) Isolated yield. c) $\overline{Mn}$ of crude products was estimated by GPC based on PSt. d) PTS=*p*-toluenesulfonic acid; PPTS=pyridinium *p*-toluenesulfonate. e) Structure was confirmed. f) Crosslinked polymer. g) Separated by preparative GPC.

Furthermore, The obtained polymers may be expected to be hydrolyzed easily because they have sensitive acetal groups to acid in the backbone. To a solution of the polymer in acetone was added 0.1 N-HCl at room temperature and the mixture was stirred at room temperature. The hydrolysis proceeded smoothly to form xylylene glycol and acrolein quantitatively.[5)]



In summary, we demonstrated in the present paper that **1**, a bis(alkoxyallene)s could be applied to cationic polyaddition with diol to afford a functional polyacetal having vinyl groups in the side chain. The obtained polymer was hydrolyzed in aqueous acid to regenerate the starting diol and acrolein. Further works on the polyaddition of other bisallenes and diols as well as applications of the resulting polymers functional materials are in progress.

References

1) For reviews, see: T. Endo and T. Yokozawa, *Koubunshi*, **41**, 82 (1992); T. Yokozawa, *Kagaku To Kogyo*, **44**, 218 (1991).

2) T. Yokozawa, E. Sato, and T. Endo, *Chem. Lett.*, **1991**, 823.

3) S. Hoff, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **87**, 1179 (1968).

4) The reaction of benzyloxyallene and an equimolar benzyl alcohol was carried out at -10 °C with a catalytic amount of PTS (0.25 mol%) in CH_2Cl_2 to afford the acetal formed by addition of alcohol to the internal carbon-carbon double bond of allene in 97% yield. ^{1}H NMR ($CDCl_3$, TMS) δ 7.27 (s, 10H) 6.23-5.03(m, 4H) 4.60 (s, 4H) ; ^{13}C NMR ($CDCl_3$) δ 138.0, 135.0, 128.0, 127.4, 127.2, 118.4, 99.5, 66.5 ; IR (neat) 1209, 1025 cm^{-1}

5) The hydrolysis of the obtained polymer ($\overline{M}n$=3200) was carried out at room temperature with 0.1 N-HCl in acetone. After the reaction, the produced acrolein in the mixture was monitored by gas chromatography. Further the mixture was washed with water, followed by evaporation to obtain colorless viscous xylylene glycol in 98% yield.

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