Polymer Bulletin 4, 491–495 (1981)

Polymer Bulletin

Copolymer Composition in the Cyclocopolymerization of Diallyl Ether with Sulfur Dioxide

Kiyohisa Fujimori

Department of Chemistry, University of New England, Armidale, NSW 2351, Australia

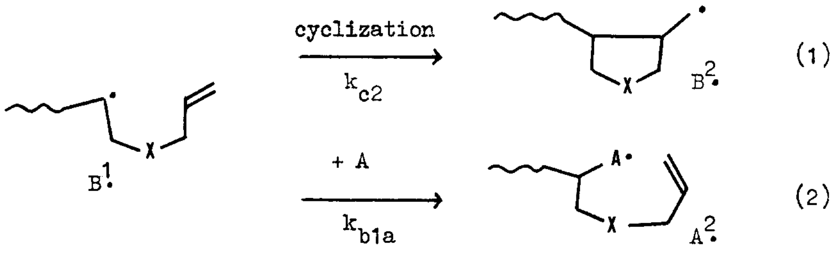
SUMMARY

The copolymer composition equation based on the intramolecular cyclization and the intermolecular propagation model for the copolymerization of 1,6-dienes and monoolefins was applied to the radical copolymerization of diallyl ether and sulfur dioxide. The ratio of the rate constants of the heteropropagation and the cyclization of the uncyclized diallyl ether radical, r_b, was 0.72±0.10 in benzene and 0.60±0.10 in DMSO at 45°C.

INTRODUCTION

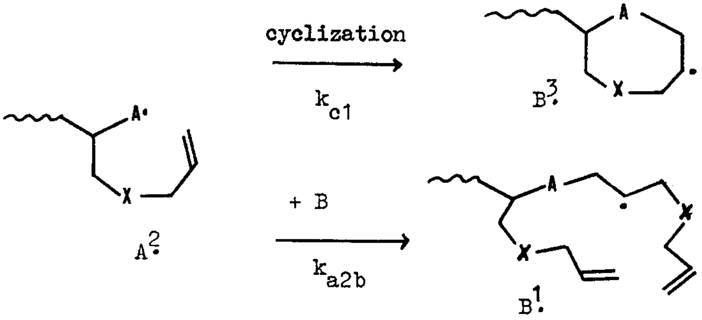
Diallyl monomers and monoolefins were shown to cyclocopolymerize (AMEMIYA et al, 1977; FUJIMORI and KHOO, 1978). The course of the cyclocopolymerization was thought to involve intra- and intermolecular propagation steps. The copolymer composition equation based on this model has been proposed for the cyclocopolymerization of the monoolefin(A) and the 1,6-diene(B) that are incapable of homopolymerizing (FUJIMORI, 1978).

The radical of the diallyl monomer $B^1\cdot$ is thought to do either an intramolecular cyclization to form a cyclic radical $B^2\cdot$ or an intermolecular reaction to form the monoolefin radical $A^2\cdot$.



The monoolefin radical $A^2\cdot$ may attack the pendant allylic group of the penultimate unit, or it may undergo reaction with another molecule of the diallyl monomer, which would result in the production of pendant allylic groups.

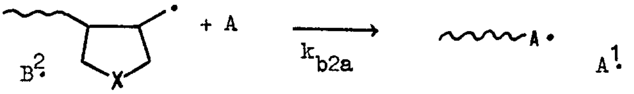
0170-0839/81/0004/0491/$01.00



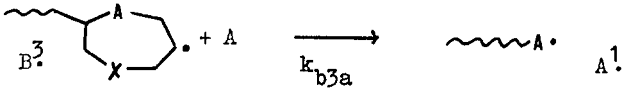
(3)

(4)

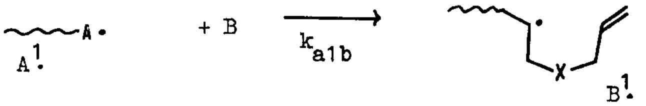
As the monoolefin and the diallyl monomer do not homopolymerize, they undergo only cross propagations except for the possibility of the intramolecular cyclization of $B^1\cdot$ radical (Eqn.(1)).



(5)



(6)



(7)

The copolymer composition equation based on this model is:

$$\frac{d[A]/dt}{d[B]/dt} = n = \frac{(\ r_a[B] + 1\ )(\ [A] + 1/r_b\ ) + [A]}{(\ r_a[B] + 1\ )(\ [A] + 1/r_b\ )} \qquad (8)$$

where, n is the mole ratio of A and B units in the copolymer, [A] and [B] are the molar concentrations of the monomers, and $r_a = k_{a2b}/k_{c1}$ and $r_b = k_{b1a}/k_{c2}$, which are the ratios of the rate constants for the intermolecular propagation and the intramolecular cyclization.

Since the Equation (8) has been applied only to the maleic anhydride-diallyl ether and fumaronitrile-diallyl ether systems so far, the copolymerization of sulfur dioxide and diallyl ether(DAE) was carried out and the composition was analyzed by Equation (8).

EXPERIMENTAL

DAE(Tokyo Kasei) was fractionally distilled after drying over Na_2SO_4. Reagent grade SO_2(CIG) was used as received. Benzene and dimethyl sulfoxide(DMSO) solutions of SO_2 were prepared and the concentration of SO_2 was determined by mixing the SO_2 solution with 1M NaOH solution and back-titrating the mixture with 1M HCl.

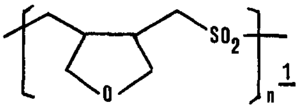
The polymerization was carried out at 45 ± 0.1°C in sealed glass tubes in which DAE, the SO_2 solution, the solvent and azobisisobutyronitrile were placed. The reaction mixture was degassed by the freeze-thaw method and the glass tube was sealed under vacuum (10^{-3}mm Hg). The polymer prepared in benzene was separated and purified by reprecipitating it in diethyl ether and the polymer prepared in DMSO was reprecipitated in 1M NaCl aqueous solution, washed with water which was replaced with acetone, and vacuum dried over $CaCl_2$. The conversion was measured gravimetrically.

The sulfur content of the polymers was measured by the Schöniger's method(SCHÖNIGER,1956); about 10 mg of the sample was burnt in O_2 with Pt catalyst in a flask that contained 5 ml of water and a few drops of 100 volume H_2O_2. The mixture was shaken vigorously for 15 minutes and the content was gently boiled for a few minutes. The sulfuric acid formed was directly titrated with 0.05M NaOH with phenolphthalein. The copolymer composition was calculated on the basis of the sulfur content.

Perkin-Elmer Type 597 IR spectrophotometer and Varian Type 100 60 MHz NMR spectrophotometer were used to register the spectra.

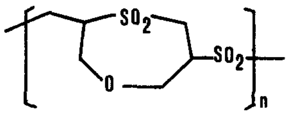
RESULTS AND DISCUSSION

The copolymer precipitated in benzene as the polymerization proceeded. A slightly crosslinked polymer was obtained possibly due to the precipitation of the propagating radical. In DMSO solution, the polymerization was homogeneous. The copolymer was soluble in DMSO,DMF and concentrated H_2SO_4 but insoluble in less polar solvents. The IR spectra of the copolymers obtained in DMSO and those obtained in benzene showed identical peaks that indicated complete absence of absorptions for C=C unsaturation. The absorption in the copolymers at 1115(s) and 1290(s) cm^{-1} indicated the presence of sulfone group. The ^{1}H-NMR spectra of the copolymer from the viscous solution in conc.H_2SO_4 at 37 °C showed broad peaks centered at 4.0δ for the protons next to the ether oxygen, and at 3.0δ for the protons adjacent to the sulfone group. Clusters of multiple peaks centered at 2.20δ for the tertiary protons and at 1.95δ for the methylene protons were present. These are consistent with the proposed repeating units of 1 and 2.



1

1:1 repeating unit



2

1:2 repeating unit

The copolymerization was carried out to a limit in benzene. As shown in Fig.1, the limiting yield was in between the theoretical limits of 1:1 and 1:2 (=DAE:SO_2) regular copolymerizations. This corresponds to the simultaneous formation of repeating units such as 1 and 2.

Since the copolymer was soluble and lacked C=C unsaturation, it is thought that the reaction such as (4) is absent, i.e., r_a= 0. The Equation (8) reduces to be:

$$n = (2r_b[A] + 1)/(r_b[A] + 1) \qquad (9)$$

The copolymer composition which was calculated on the basis of the

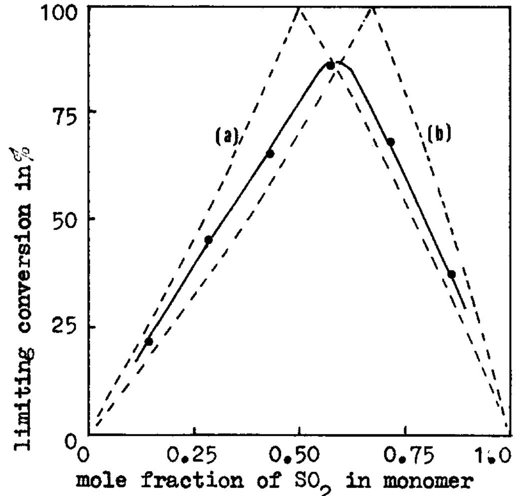


Fig.1. The limiting conversion in the copolymerization of DAE with SO_2 in benzene: 56 hours, at 45°C. $[DAE+SO_2]$ = 1.65M, [AIBN]=1.22x10^{-2}M. (a)The theoretical limiting conversion for 1:1 copolymer. (b)The theoretical limiting conversion for 1:2 copolymer.

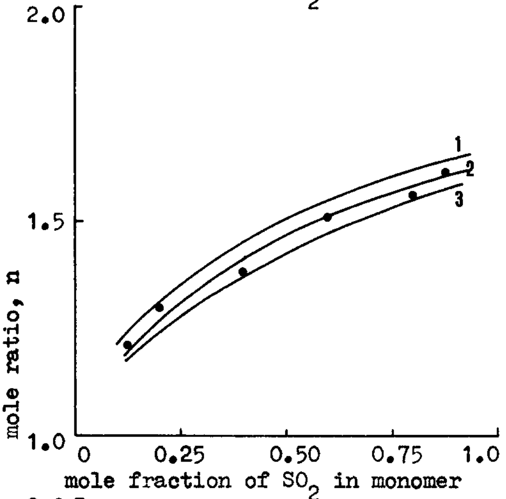


Fig.2. The copolymer composition of DAE-SO_2 copolymer prepared in benzene at 45°C. $[DAE+SO_2]$ =1.65M, [AIBN]=2.44 x10^{-2}M.
n = d[SO_2]/ d[DAE] in polymer. The solid lines are calculated by Eqn.(9) for r_b= 0.80(1), r_b=0.72(2) and r_b =0.62(3).

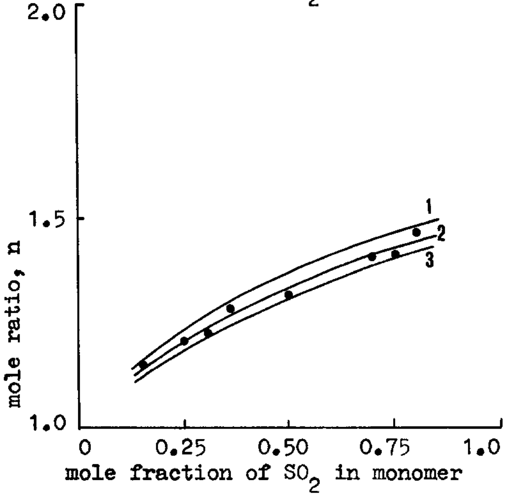


Fig.3. The copolymer composition of DAE-SO_2 copolymer prepared in DMSO at 45°C. $[DAE+SO_2]$=1.67M, [AIBN]=2.47 x10^{-2}M.
n = d[SO_2]/ d[DAE]in polymer. The solid lines are calculated by Eqn.(9) for r_b= 0.70(1), r_b=0.60(2) and r_b =0.55(3).

sulfur contents is shown in Fig.1 and Fig.2. In all cases the conversion was well below 10 %. The agreement between the calculated curves by Equation (9) with the experimental results indicate that the repeating unit 1 is formed through the Reactions (1) and (5), and the repeating unit 2, through (3) and (6); the propagation involves the intramolecular cyclization and intermolecular catenations.

The r_b values, which are the ratios of the rate constant of Reaction (2) to that of Reaction (1), in DMSO and in benzene were 0.60 ± 0.10 and 0.72 ± 0.10, respectively. Since the electrostatic interaction between $B'\cdot$ radical and the electron-accepting SO_2 is more pronounced in less polar benzene than in DMSO, it appears that the transition state of the Reaction (2) is better stabilized in benzene. The r_b values show that the cyclization of the DAE radical, $B'\cdot$, is more dominant reaction compared to its heteropropagation with SO_2 despite the fact that DAE does not homopolymerize. Solomon et al proposed that the proximity of the pendant double bond to the intramolecular radical allowed the cyclization of the $B'\cdot$ radical kinetically (SOLOMON,HAWTHORNE,1976). Butler proposed an electronic interaction between the $B'\cdot$ radical and its pendant double bond to explain the cyclization in the polymerization of 1,6-dienes (BUTLER,1960). The r_b is the measure of reactivity of monoolefin toword the uncyclized radical of DAE. In benzene, the r_b was 0.35 for the DAE-maleic anhydride system and 0.15 for the DAE-fumaronitrile system at 60°C (FUJIMORI,1978), while the DAE-SO_2 system gave r_b=0.72 at 45°C. Both the steric and polar factors seem to play roles; the sterically less bulky SO_2 has an advantage to react with $B'\cdot$, and more polar maleic anhydride(Alfrey-Price e=2.25, Q=0.23) shows larger reactivity with the $B'\cdot$ radical than fumaronitrile(e=1.96,Q=0.80(YOUNG,1964)).

REFERENCES

AMEMIYA,Y.,KATAYAMA,M. and HARADA,S.:Makromol.Chem.178,2499(1977)
BUTLER,G.B.:J.Polym.Sci.48,279(1960)
FUJIMORI,K. and KHOO,M.:Makromol.Chem.179,859(1978)
FUJIMORI,K.:Makromol.Chem.179,2867(1978)
SCHONIGER,W.:Mikrochim.Acta 1956,869
SOLOMON,D.H. and HAWTHORNE,D.G.:Macromol.Sci.,Rev.Macromol.Chem.15, 143(1976)
YOUNG,L.J.:in HAM,G.E. ed. Copolymerization, New York,Interscience 1964, page 845

Received March 16, 1981
Accepted March 23, 1981