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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Aso, Chuji, Kunitake, Toyoki and Ando, Shoji(1971) 'Studies on the Polymerization of Bifunctional Monomers. XIX. Radical Cyclopolymerization of Divinylformal', Journal of Macromolecular Science, Part A, 5: 1, 167 – 180

To link to this Article: DOI: 10.1080/00222337108061031

URL: <http://dx.doi.org/10.1080/00222337108061031>

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Studies on the Polymerization of Bifunctional Monomers. XIX. Radical Cyclopolymerization of Divinylformal*

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SUMMARY

Radical polymerizations of divinylformal were carried out with AIBN initiator in several solvents. In many solvents (benzene, cyclohexane, acetonitrile, DMSO, etc.), the polymers consisted of the cyclized monomer unit and 5 to 8% of the pendant formate group. The amounts of the residual vinyl group were quite small in these solvents. The formate group was probably formed by the hydrogen migration and the subsequent ring scission of the cyclic propagating radical. On the other hand, a polymer obtained in CS₂ contained about 30% of the pendant vinyl group but no formate group. In addition, the carbon and hydrogen contents of this polymer were lower than expected, and sulfur was detected instead. The polymerization in benzene-CS₂ mixtures indicated a much stronger influence of CS₂ than benzene. These results suggest that CS₂ molecules interact strongly with the propagating radical to the extent that it can be incorporated into polymer.

*Contribution No. 199 from this department. Presented at the 5th IUPAC Microsymposium on Macromolecules, Prague, Czechoslovakia, September, 1969.

INTRODUCTION

Radical cyclopolymerization of divinyl acetals has been studied by several groups of investigators in recent years [1-4]. In particular, Minoura et al. [3] and Arbuzova et al. [4] showed that polydivinyl acetals contained three structural units: the six-membered ring, the five-membered ring, and the unit with the pendant vinyl group.

In order to elucidate the mode of the intramolecular cyclization of these monomers, telomerization of divinylformal in CHCl_3 was carried out in these laboratories [5], following the earlier studies on telomerization of diallyl ether [6] and divinyl ether [7]. In all these telomerizations five-membered ring adducts were produced in preference to the six-membered counterparts. On the basis of these results the probable solvent effect on the adduct structure in the telomerization of divinylformal was discussed [5].

In the present investigation, divinylformal was polymerized in several solvents, and the isomerization of the propagating radical and the remarkable solvent effect of CS_2 on the radical reactivity were observed. The solvent effect on the ring size of the structural unit was not included in the present investigation.

EXPERIMENTAL

Materials

Divinylformal was prepared, as previously described [3, 5], by alkali fusion of β, β' -dichloroethylformal which was formed from formalin and ethylene chlorohydrin. The monomer was purified by repeated distillation and the purity was confirmed by gas chromatography. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified by the conventional methods.

Procedures

Polymerizations were carried out with AIBN initiator in sealed ampoules at 70°C . The ampoules were sealed in vacuo after degassing by several cycles of freeze-and-thaw under nitrogen. After a given polymerization period, the reaction mixture (approximately 20 ml) was poured into excess light petroleum ether and the polymer was recovered as a white powder. Reprecipitation was carried out from benzene and methanol, and the

polymer was dried in vacuo. The amount of the insoluble fraction in benzene was small. The sulfur content in polymer was determined by the Schoniger's combustion method [8].

RESULTS

Table 1 gives the polymerization results in several solvents. The polymerizations were generally slow under the given condition and 10 to 12 hr were required to attain appropriate conversions. Figure 1 shows IR spectra of polydivinylformal obtained in benzene and in CS_2 . These spectra are quite different in some respects. The polymer obtained in benzene does not possess peaks at 1630 and 1650 cm^{-1} where the vinyl peaks of the monomer are present. Strong, broad peaks at 950 to 1200 cm^{-1} are due to the acetal linkage formed by cyclopolymerization. An unexpected peak appears at 1730 cm^{-1} , which is probably due to the carbonyl group. Thus, apart from the carbonyl peak, this polymer must contain the cyclized unit alone. On the other hand, the polymer obtained in CS_2 gives peaks (1630 and 1650 cm^{-1}) attributable to the pendant vinyl group and, therefore, this polymer apparently contains a considerable amount of the uncyclized

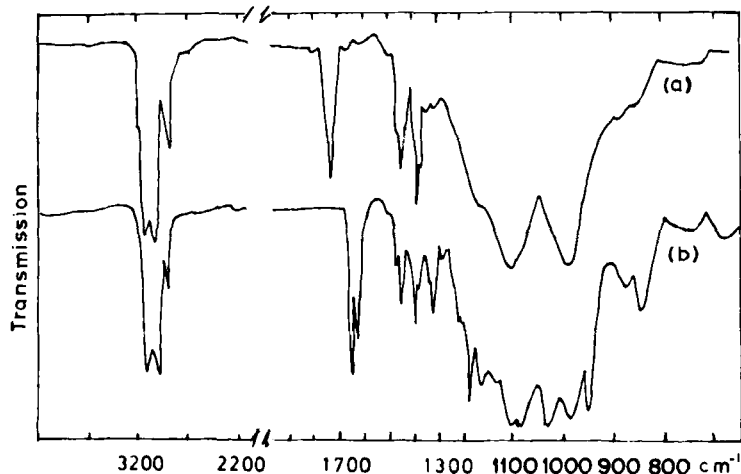


Fig. 1. IR spectra of polydivinylformal obtained in benzene (a) and in CS_2 (b). Solvent, CCl_4 .

Table 1. Polymerization of Divinylformal in Several Solvents. Polymerization temperature, 70°C. Monomer concentration, 2.6 mole/l. Initiator, AIBN, 1.8×10^{-2} mole/l

Solvent	Polymerization time (hr)	Conversion (%)	Pendant vinyl group (%) ^a determined at		Pendant carbonyl group (%) ^b determined at 1730 cm ⁻¹	MWC
			1650 cm ⁻¹	1630 cm ⁻¹		
Benzene	20	38.0	0	0	5.2	5000
CS ₂	20	7.2	33d(38)	27d(31)	0	2000
DMSO	20	15.1	0	0	7.3	—
DMF	10	11.7	0	0	6.3	—
Cyclohexane	10	27.7	0	0	8.1	—
CH ₃ CN	10	31.2	2.2	2.0	5.3	—

^aThe monomer was used as the reference compound.

^bMethyl formate was used as the reference compound.

^cMeasured in benzene with a vapor pressure osmometer (Mechrolab, Model 301A).

^dThese values were determined without assuming the presence of the CS₂ unit. The values in parentheses indicate the mole % of the functional group for the divinylformal unit (CS₂ unit excluded).

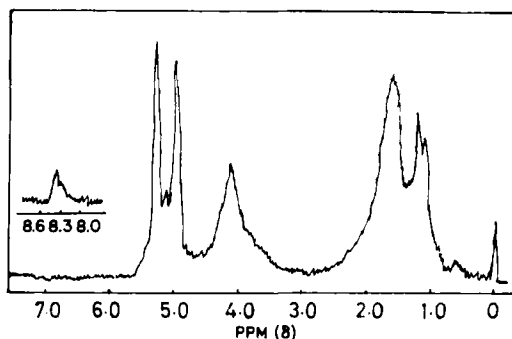


Fig. 2. NMR spectrum of polyvinylformal obtained in benzene. Solvent, CCl_4 ; internal standard, TMS. The insert has been multiplied by a factor of 4.

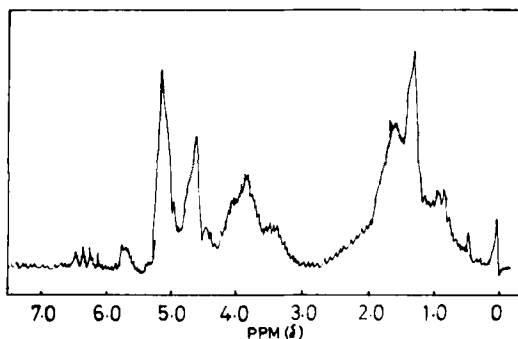


Fig. 3. NMR spectrum of polyvinylformal obtained in CS_2 . Solvents, CCl_4 ; internal standard, TMS.

unit. The carbonyl peak is absent. The IR spectra of the polymers obtained in other solvents were much the same as that of the benzene polymer.

The NMR spectra of the polymer samples obtained in benzene and in CS_2 are given in Figs. 2 and 3, respectively. The spectrum of the benzene polymer shows three major peak groups at 1.1 to 2.0 ppm, at 3.1 to 4.4 ppm, and at 4.8 to 5.3 ppm. They can be assigned to aliphatic methylene protons, to methyl and methylene protons adjacent to one ether oxygen, and to acetal methylene protons, respectively. These peaks are consistent with the cyclic structure generated by cyclopolymerization. A small but definite peak is present at 8.35 ppm. This peak can be assigned to the formate proton, considering the presence of the fairly strong IR peak at 1730 cm^{-1} . The NMR

Table 2. Structure of the Polymer obtained in Benzene-Carbon Disulfide Mixtures. Polymerization condition, 70°C, 20 hr. Monomer concentration, 2.6 mole/l. Initiator, AIBN, 1.8×10^{-2} mole/l

Solvent $\text{CS}_2/(\text{CS}_2 + \text{C}_6\text{H}_6)$ (vol %)	Pendant vinyl group (%) ^a determined at		Pendant carbonyl group (%) ^b determined at		Conversion (%)	Elemental analysis ^c		CS_2 unit content ^d (%)
	1650 cm^{-1}	1630 cm^{-1}	1730 cm^{-1}			C%	H%	
0	0	0	5.2		38.0	60.25	8.14	0
0.7	8.2(8.2)	6.3(6.3)	1.3(1.3)		19.2	59.04	7.91	0
3.6	12	8.7	0		13.0	—	—	—
7.1	14(14)	11(12)	0		11.1	57.78	7.79	6.5
14.3	15	13	0		9.5	—	—	—
21.4	18(20)	16(17)	0		7.2	57.18	8.05	8.2
28.6	22(24)	19(21)	0		6.4	56.63	7.55	9.8
100.0	33(38)	27(31)	0		7.2	54.07	6.99	16.9

^aSee Footnotes a and d, Table 1.

^bSee Footnotes b and d, Table 1.

^cCalculated for $(\text{C}_5\text{H}_8\text{O}_2)_n$: C, 59.98%; H, 8.05%.

^dEstimated from the respective carbon content.

spectrum of the CS₂ polymer (Fig. 3) is generally similar to that of the benzene polymer, suggesting the predominant presence of the cyclized structure. However, the presence of the vinyl group is also apparent from the characteristic peak group at 6 to 6.5 ppm. The formate proton is absent.

The amounts of the pendant vinyl group and the formate group were determined as given in Table 1 from comparison of the IR peak intensities of the polymer with those of monomer and methyl formate, respectively. The peak area of the formate proton was 2.2% of that of the acetal proton (—OCH₂O—) in Fig. 2. Thus, the amount of the formate group is 4.2% of the monomer unit. This value is in reasonable agreement with that determined from IR spectroscopy. For all the solvents except for CS₂, the polymer contained approximately the same amount (5-8%) of the formate group and is completely cyclized otherwise. Carbon disulfide is a very particular solvent in this respect, and the CS₂ polymer contained 30 mole % of the pendant vinyl group, and the formate group was absent. The rate of polymerization was much slower in CS₂ than in other solvents, and the molecular weight of the polymer decreased in CS₂ as compared with that in benzene solvent.

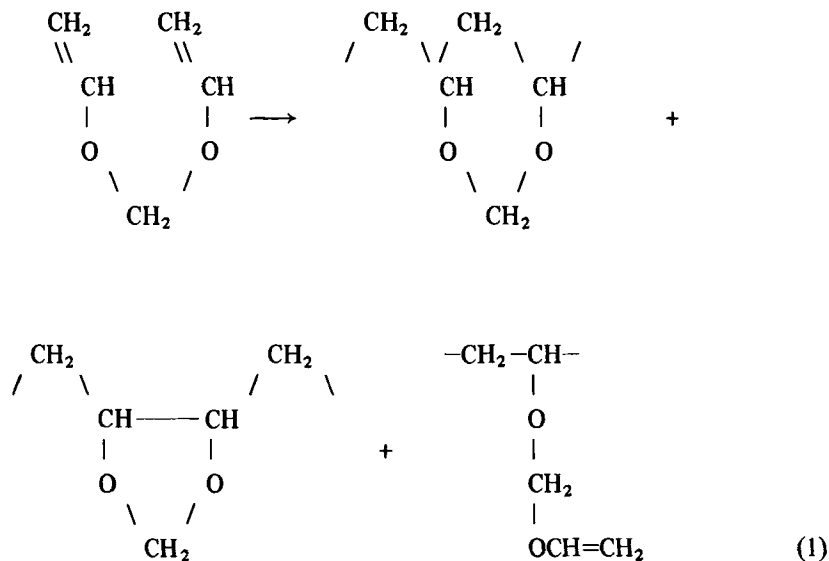
Since the polymer obtained in CS₂ was very different from those in other solvents, the influence of CS₂ solvent was further studied by carrying out the polymerization in mixtures of benzene and CS₂. The results are given in Table 2. The influence of CS₂ is very remarkable. By adding 0.7 vol % CS₂ to benzene solvent, the vinyl group in polymer increased from 0 to about 7%, and the formate group decreased from 5.2 to 1.3%. On further addition of CS₂, the amount of the pendant vinyl group increased gradually and the formate group became undetectable. The rate of polymerization showed a gradual decrease with the increase in the CS₂ content in the solvent mixture.

An interesting fact was found when elemental analyses were carried out for the polymer obtained in these solvent mixtures. The carbon and hydrogen analyses of the benzene polymer agreed well with those expected for polydivinylformal. However, both of the carbon and hydrogen contents decreased with the increase in the amount of CS₂ in the solvent mixture. Since sulfur was detected in the polymers obtained in CS₂-containing media, the deviation in the elemental analyses was probably caused by incorporation of CS₂ into polymer. The contents of CS₂ in the polymer as estimated from the carbon content are given in Table 2.

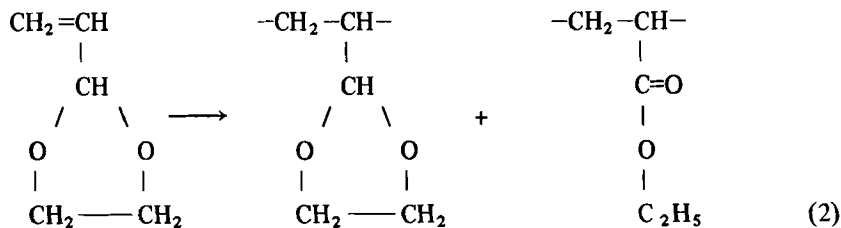
DISCUSSION

Isomerization Propagation

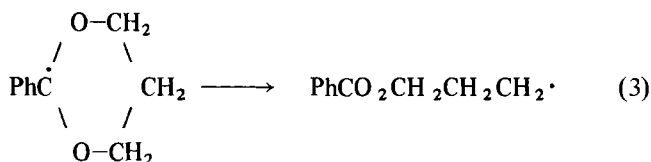
In the previous publications on the radical polymerization of divinylformal [3, 4], three structural units were considered to exist in the polymer.



As is clear from the polymerization data given above, however, polydivinylformals obtained in most solvents were shown to contain the formate group in addition to the cyclized and uncyclized units. In the absence of any evidence for oxidation, the formate group must be produced by isomerization. An example of isomerization polymerization was given by Kagiya and co-workers [9], who found that polymerization of 2-vinyl-1,3-dioxolane by AIBN or by γ -ray irradiation yielded a polymer containing the isomerized unit.



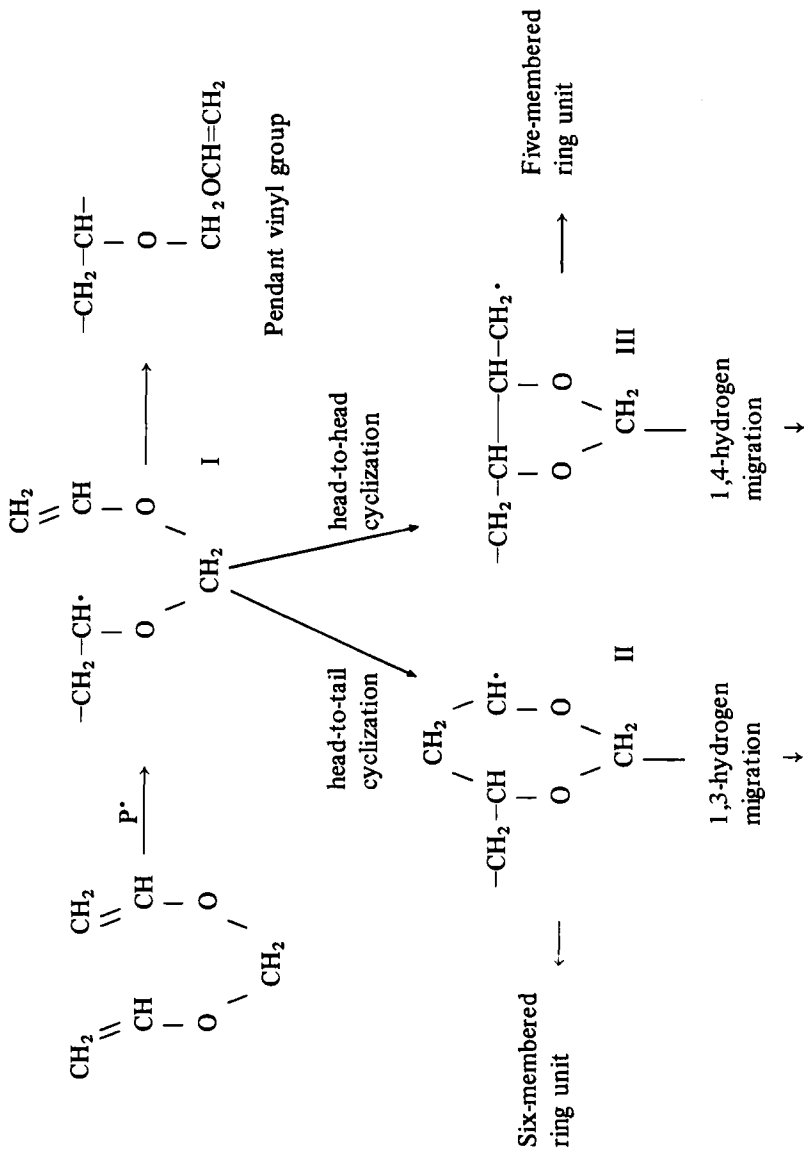
Formation of the isomerized unit was attributed to 1,3-hydrogen migration, though the course of isomerization was not described. On the other hand, the hydrogen abstraction from the acetal carbon of cyclic acetals are known to lead to the ring-opening [10-12]. One of the examples is given in Eq. (3) [10].

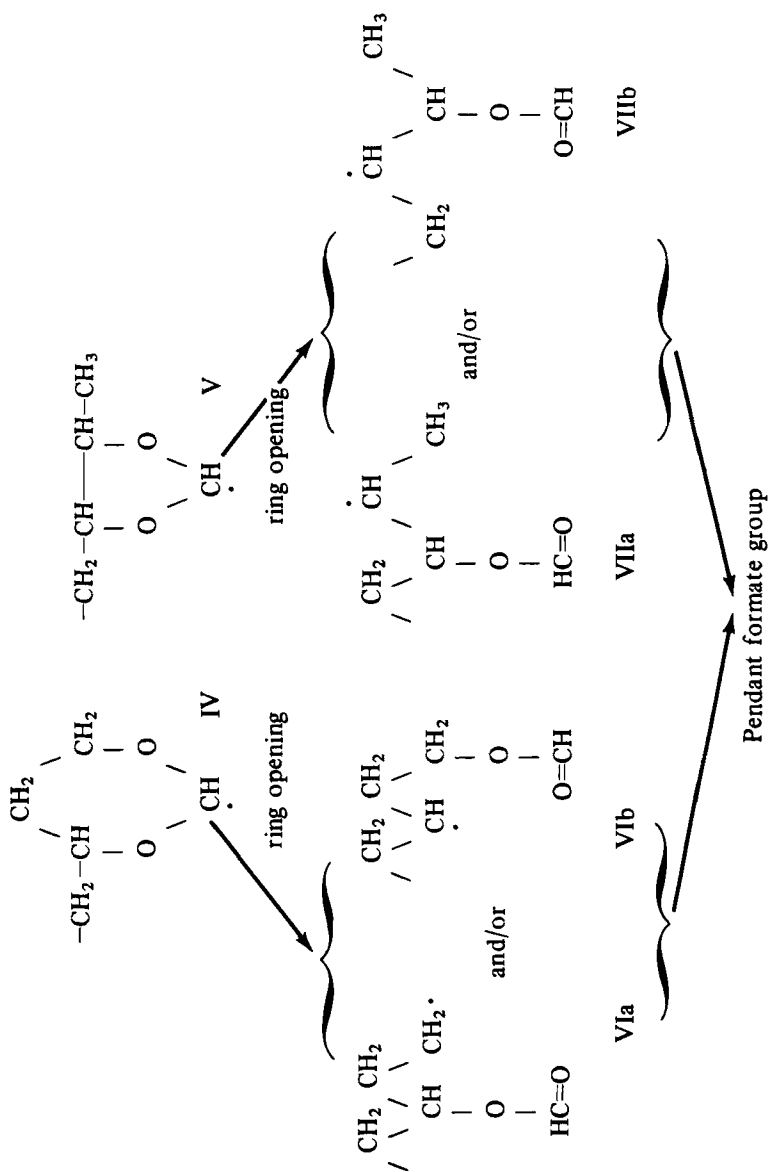


Thus, the formate group in polydivinylformal was probably formed by hydrogen migration in the propagating cyclized radical. The propagation scheme of divinylformal in most solvents, therefore, can be tentatively shown as in Scheme 1.

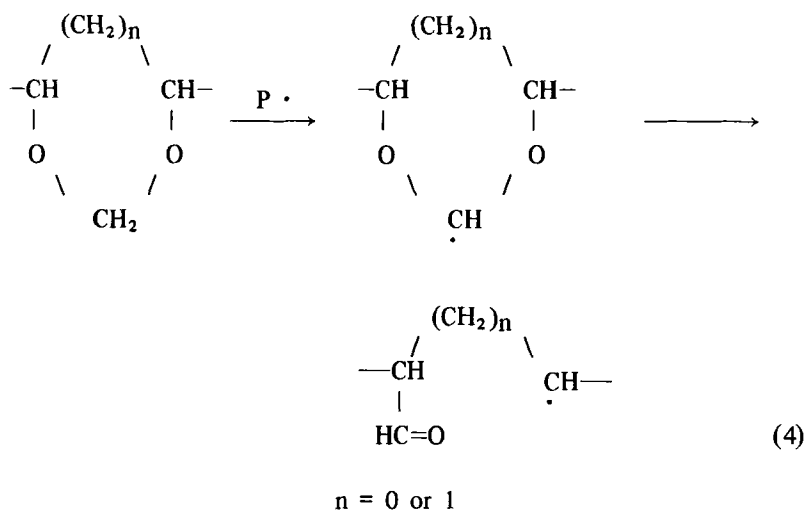
The monomer first reacts with the propagating radical to form an uncyclized radical (I). This radical can either add to a monomer molecule, producing a pendant vinyl group in polymer, or cyclize to five- and/or six-membered cyclic radicals. The propagation from the cyclized radicals gives rise to five and/or six-membered ring units in polymer. For the polymer obtained in solvents other than CS_2 , the amounts of the pendant vinyl group were very small if any. Therefore, the intramolecular cyclization occurs preferentially in most solvents. Although both of the five- and six-membered rings are probably contained in the polymer, referring to the results of the previous investigations [3, 4], the effect of solvents on the mode of cyclization is not clear, as the size of the ring unit is yet to be determined. The cyclized radicals (II, III) can abstract the labile acetal hydrogen to give new radicals IV and V, which then undergo the ring cleavage, yielding radicals containing pendant formate groups (VI, VII). The detail of formation of the formate group cannot be described at the present time. For example, it is not clear whether the formate group is derived from II, or III, or from both. There may be a considerable difference in the tendency of hydrogen migration between II and III. There should also be difference in the direction of the ring opening (VIa or VIb, VIIa or VIIb).

The formate group can possibly be formed by the chain transfer to polymer, as in Eq. (4). This reaction will lead to branching or cross-linking. Though contribution of this reaction to formation of the formate group cannot be excluded altogether, its importance is probably small because the





Scheme 1.



molecular weights of the polymer are rather small and no cross-linking occurred under the normal polymerization condition.

Solvent Effect of CS₂

Table 1 shows the peculiar characteristics of CS₂ as solvent. Apart from CS₂, the polymer structure did not change appreciably for a variety of solvents including cyclohexane and acetonitrile. Thus, the structural variation cannot be associated with the change in the polar character of solvents. Carbon disulfide is known to exert a large solvent effect on the reactivity of free radicals. Russell found that CS₂ was most effective in enhancing the selectivity of the chlorine atom in chlorination of 2,3-dimethylbutane [13]. The reactivity ratios in the radical copolymerization of styrene and acrylonitrile in CS₂ were quite different from those in other solvents [14]. These results can be explained by considering a strong interaction of CS₂ molecules with radicals. Similarly, the propagating divinylformal radical will be preferentially solvated by CS₂ in CS₂-benzene mixtures (Table 2), and is much less reactive in CS₂ than in other solvents, as reflected in the diminished rate of polymerization (Table 1).

When the uncyclized radical I interacts strongly with CS₂, the cyclization tendency may decrease from either or both of the following two reasons: 1) In the radical cyclopolymerization of some divinyl monomers, intramolecular cyclizations possess higher activation energies than the

corresponding intermolecular propagation [15, 16]. Therefore, stabilization of the radical due to solvation can result in a decrease in the extent of cyclization. 2) The predominant cyclization may be attributed at least in part to the interaction of the radical with the neighboring vinyl group. In that case the presence of CS_2 solvent will reduce the cyclization because CS_2 molecules can solvate the radical in place of the neighboring vinyl group.

Carbon disulfide should similarly interact with the cyclized radical to make it less reactive. Thus, the lack of the formate group is conceivably caused by the decreased reactivity of the cyclized radical and the resulting suppression of the hydrogen migration.

The probable incorporation of CS_2 into the polymer is an interesting phenomenon. Since the amount of the CS_2 unit reached 17 mole % and the molecular weight was 2000 for the polymer obtained in CS_2 , CS_2 may be considered to be incorporated into polymer as a comonomer.* The occurrence of CS_2 addition to the propagating radical is related to the large solvent effect displayed by CS_2 , and CS_2 molecules must be interacting strongly with the radical, irrespective of whether or not a CS_2 molecule adds to the radical.

The ring size of the cyclized unit in the polymer was not investigated in this study. As mentioned in a previous study [5], the ring size may be influenced by the nature of solvents. In particular it is interesting to study how CS_2 affects the mode of cyclization. Further studies on the solvent effect on the polymer structure are being carried out in these laboratories.

ACKNOWLEDGMENT

The authors are grateful to Mr. M. Ohtsuru for his capable technical assistance.

*Since this paper was read at the Microsymposium, the sulfur content of a polymer sample (Table 2, Run 2) was determined to be 9.9%. Assuming that this polymer consisted solely of the divinylformal unit and the CS_2 unit, the CS_2 content estimated from the sulfur content was 15 mole %, in close agreement with that estimated from the carbon content (17 mole %).

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Accepted by editor November 19, 1969

Received for publication June 29, 1970