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The Fundamental Basis for Cyclopolymerization. IX. A Cyclopolymerization Study of Certain Unsymmetrical 1,6-Heptadienes*

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ABSTRACT

In an effort to study unsymmetrical 1,6-heptadienes which may form intramolecular charge-transfer complexes and thus enhance their cyclopolymerization characteristics, 2-phenylallyl methacrylate, 2-phenylallyl-2'-carboethoxyallyl ether, methallyl methacrylate, 2-phenylallyl ether, and 2-phenylallyl methallyl ether were cyclopolymerized by free radical initiation. 2-Phenylallyl-2'-carboethoxyallyl ether polymerized by both free-radical and thermal initiation to yield cyclopolymers having little residual unsaturation and $[\eta] = 0.185$ and 0.390 dl/g, respectively. 2-Phenylallyl methacrylate led to polymer via free-radical initiation having $[\eta] = 0.264$ dl/g and containing a large amount of residual

*Presented in part before the Division of Polymer Chemistry, American Chemical Society, Houston, Texas, February 1970; taken from the Ph.D. Dissertation of Keith B. Baucom, University of Florida, 1971; for Paper VIII of this series, see J. Macromol. Sci.—Chem., A8(7), 1205 (1974).

2-phenylallyl unsaturation. 2-Phenylallyl ether led to cyclopolymers having $[\eta] = 0.125$ and 0.070 dl/g, respectively, via both free-radical and cationic initiation. Both cyclopolymers contained very little residual unsaturation. 2-Phenylallyl methallyl ether did not polymerize via free-radical initiation.

INTRODUCTION

The previous paper of this series (VIII) [1] reported the synthesis of certain unsymmetrical 1,6-heptadienes which may form intramolecular charge-transfer complexes or show electronic interaction, either in the ground or excited states, between neighboring double bonds. For comparison, all of the corresponding monoenes were prepared. A systematic UV, IR, and NMR spectral study was made of these monomers in an effort to determine the extent of such interactions if they could be observed. This study as reported in Paper VIII failed to reveal any indication of these types of interaction in these monomers. Nevertheless, these monomers were found to undergo cyclopolymerization to yield predominantly cyclic polymers. The results of this study are reported in this paper.

A number of reviews on cyclopolymerization are available [2-6]. As has been pointed out in one or more of these reviews, and in greater detail in Paper VIII of this series [1], certain aspects of the cyclopolymerization mechanism remain to be justified in terms of experimental observations. These inconsistencies involve: 1) experimental results which show that k_c , the cyclization rate constant, is much higher than k_p , the linear propagation rate constant (without cyclization), values of the k_c/k_p ratio ranging from 5 to 20 moles/liter [6]; 2) pseudo-second-order rate constants which indicate the intramolecular double bond concentration with respect to the neighboring radical to be from 20 to 100 moles/liter [7, 8]; and 3) in all cases of cyclopolymerization studied, the activation energy for cyclization, E_c , is greater than E_{11} , the activation energy for linear propagation, without cyclization, by >1.5 kcal/mole [6].

The unsymmetrical 1,6-heptadienes studied along with their respective monoene models are: 2-phenylallylmethacrylate (I) and its corresponding monoenes, 2-phenylallyl isobutyrate (II), β -phenyl-*n*-propyl methacrylate (III), and isobutyl methacrylate (IV); 2-phenylallyl-2'-carboethoxyallyl ether (V) and its corresponding monoenes, 2-phenylallyl isobutyl ether (VI), and 2-carboethoxyallyl isobutyl ether (VII); methallyl methacrylate (VIII) and its corresponding monoenes, isobutyl methacrylate (IV) and methallyl isobutyrate (IX); 2-phenylallyl ether (X) and its corresponding monoenes, 2-phenylallyl-2'-phenyl-*n*-propyl ether (XI), and

2-phenylallyl isobutyl ether (VI); and 2-phenylallyl methallyl ether (XII) and its corresponding monoenes, 2-phenylallyl isobutyl ether (VI), β -phenyl-n-propyl methallyl ether (XIII), and isobutyl methallyl ether (XIV).

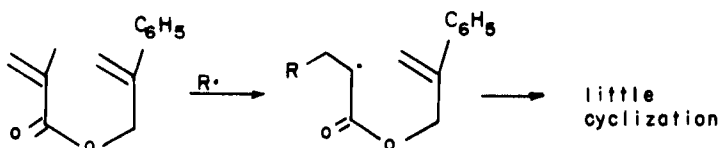
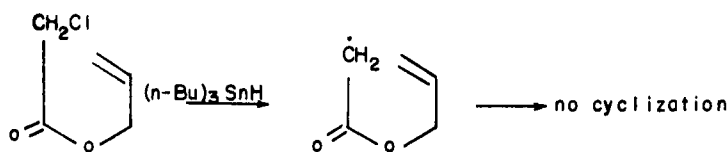
Polymerization of Monomers

2-Phenylallyl-2'-carboethoxyallyl ether (V) was polymerized in a 40% benzene solution using azobisisobutyronitrile (AIBN) as the initiator. Polymer was obtained having an intrinsic viscosity of 0.185 dl/g. Infrared spectral analysis showed that the polymer contained little residual unsaturation. The residual unsaturation was in the form of pendant 2-phenylallyl groups as indicated in the IR spectrum by absorption at 1580 cm^{-1} .

This monomer also underwent thermal polymerization during attempted fractional distillation. The polymer had an intrinsic viscosity of 0.390 dl/g. The IR spectrum was identical to that of the polymer prepared from AIBN.

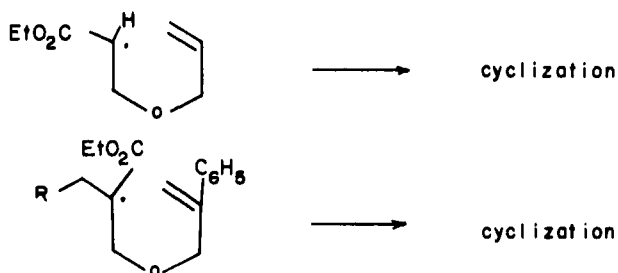
2-Phenylallyl methacrylate (I) was polymerized in a 40% benzene solution using AIBN as the initiator. Polymer was obtained having an intrinsic viscosity of 0.264 dl/g. Infrared analysis of the polymer showed a large degree of residual unsaturation. Absorption at 1580 and 1638 cm^{-1} indicated that most of the residual unsaturation was in the form of 2-phenylallyl groups. This polymer became cross-linked after sitting at room temperature for 2 days. Powell et al. [9] prepared 2-phenylallyl methacrylate and studied its polymerization. They reported that the monomer cyclized poorly and tended to give cross-linked polymer. During many attempts to fractionally distill 2-phenylallyl methacrylate, polymerization occurred, resulting in completely cross-linked gels.

In both 2-phenylallyl methacrylate (I) and 2-phenylallyl-2'-carboethoxyallyl ether (V) the residual unsaturation arises from pendant 2-phenylallyl groups. This indicates that in the polymerization the more reactive double bond, methacrylate or 2-carboethoxyallyl double bond, undergoes initiation first. This radical then reacts intramolecularly or intermolecularly. As was noted above, 2-phenylallyl-2'-carboethoxyallyl ether (V) polymerized to give a much higher percentage of cyclopolymer than did 2-phenylallyl methacrylate (I). Molecular models show that in order for the methacrylate radical to attack the 2-phenylallyl double bond intramolecularly, it must lose its resonance stabilization [7]. In the case of the 2-carboethoxyallyl radical, attack can occur on the intramolecular double bond without loss of resonance stabilization. Walling et al. [10] found that in the case of the reaction of allyl chloroacetate with tributyltin hydride, cyclization did not occur. This radical intermediate is similar to the radical produced during the polymerization of 2-phenylallyl methacrylate:



In both cases, stabilization of the radical by the ester carbonyl would be lost as the radical attacked the intramolecular double bond.

Julia [11] found that when the radical could remain stabilized as it attacked the intramolecular double bond, cyclization did result:



This is very similar to the results that were obtained during the polymerization of 2-phenylallyl-2'-carboethoxyallyl ether (V).

2-Phenylallyl ether (X) was polymerized by free-radical initiation and cationic initiation to give cyclic polymer having very little residual unsaturation with intrinsic viscosities of 0.125 and 0.070 dl/g, respectively.

2-Phenylallyl methallyl ether (XII) would not polymerize by radical initiation. This resistance to polymerization reflects the instability of the radical formed by initiation on the methallyl group. The results of the polymerization studies are shown in Table 1.

One of the purposes of this work was to compare the relative tendency of cyclization of 2-phenylallyl methacrylate (I) and 2-phenylallyl-2'-carboethoxyallyl ether (V). There was a dramatic

TABLE 1. Polymerization of Monomers

Monomer	Initiator	Concentration by weight	Solvent	% Conversion	$[\eta]$ (dl/g)
2-Phenylallyl- methacrylate	1% AIBN	40%	C ₆ H ₆	28.4	0.262
2-Phenylallyl-2'- carboethoxyallyl ether	Thermal	Neat		100	0.390
2-Phenylallyl-2'- carboethoxyallyl ether	1% AIBN	40%	C ₆ H ₆	27	0.148
2-Phenylallyl ether	1% AIBN	50%	C ₆ H ₆	4.8	0.125
2-Phenylallyl- methallyl ether	1% AIBN	50%	C ₆ H ₆	-	-

difference in the degree of cyclization that occurred. 2-Phenylallyl-2'-carboethoxyallyl ether (V) had very little residual unsaturation in the form of pendant 2-phenylallyl groups, while 2-phenylallyl methacrylate (I) had a large degree of residual unsaturation in the form of 2-phenylallyl groups. The effect of the carbonyl being in the ring seems to have a dramatic effect as was discussed earlier [6].

It was noted earlier that a comparison should be made between the cyclization of 2-phenylallyl methacrylate (I) and of 2-phenylallyl-2'-carboethoxyallyl ether (V) and the free-radical copolymerization of methyl methacrylate and α -methylstyrene. It was noted that methyl methacrylate radical reacts with α -methylstyrene twice as fast as it reacts with methyl methacrylate, and α -methylstyrene radical reacts seven times as fast with methyl methacrylate as it reacts with α -methylstyrene. It was thought that this tendency would result in an increase in the degree of cyclization in the above dienes. It has been observed that 2-phenylallyl-2'-carboethoxyallyl ether (V) does indeed give a high degree of cyclization, but 2-phenylallyl methacrylate (I) does not. The high tendency for methyl methacrylate radical to attack α -methylstyrene does not extend to the case of 2-phenylallyl methacrylate (I). This factor is apparently overcome by electronic or steric effects.

It was also shown that 2-phenylallyl ether undergoes free radical cyclopolymerization, leaving little residual unsaturation. This is in direct contrast to the well-known fact that α -methylstyrene will not homopolymerize by free-radical polymerization. It once again points out the increased reactivity of diene systems compared to the corresponding monoene systems.

EXPERIMENTAL

Equipment and Data

All temperatures are reported uncorrected in degrees centigrade. Nuclear magnetic resonance spectra were obtained on a Varian A-60A Analytical NMR Spectrometer. The chemical shifts were measured in deuteriochloroform and carbon tetrachloride using tetramethylsilane as an internal reference. Infrared spectra were obtained with a Beckman IR-8 Infrared Spectrophotometer or a Beckman IR-10 Infrared Spectrophotometer. Melting point determinations were performed in open capillary tubes in a Thomas-Hoover melting point apparatus. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee and by PCR, Inc., Gainesville, Florida.

Polymerization of 2-Phenylallyl Methacrylate (I)

Charged to a polymerization tube were 0.808 g (0.004 mole) 2-phenylallyl methacrylate, 1.212 g benzene (40% monomer by weight), and 8 mg AIBN. The polymerization tube was attached to a vacuum manifold and frozen in Dry Ice acetone. The tube was then evacuated to full pump vacuum. The monomer and solvent solution was degassed by the freeze-thaw method. The polymer tube was then sealed under full pump vacuum. The sealed tube containing monomer, solvent, and initiator was placed in a 60°C bath. At the end of an 18-hr period the tube was removed from the bath and opened. The polymer solution was poured into excess methanol which precipitated the polymer. The yield of dry polymer was 0.2298 g or 28.4% conversion. The intrinsic viscosity in benzene at 30°C was 0.264 dl/g.

The IR spectrum (KBr) of the polymer gave absorption bands at 3460(broad), 3100(w), 3070(m), 3020(m), 3000(m), 2960(m), 1725(vs), 1640(m), 1603(w), 1580(w), 1498(m), 1450(s), 1390(m), 1320(w), 1295(m), 1250(s), 1150(broad) 1030(w), 1005(w), 975(w), 910(m), 840(w), 810(w), 775(s), 755(s), and 700(s) cm^{-1} .

Analysis: Calculated for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20; H, 6.98. Found: C, 72.81; H, 6.45.

Radical Polymerization of 2-Phenylallyl-2'-carboethoxyallyl Ether (V)

Charged to a polymer tube were 0.984 g (0.004 mole) of 2-phenylallyl-2'-carboethoxyallyl ether, 10 mg AIBN, and 1.476 g benzene giving a 40% solution. The tube was frozen and degassed by the freeze-thaw method at full pump vacuum. After the tube was sealed, it was placed in a polymerization bath at 60°C. After 18 hr the polymer was precipitated from solution with methanol to give 0.2663 g (27.0%) polymer having an intrinsic viscosity of 0.148 dl/g in benzene at 30°C.

The IR spectrum (KBr) gave absorption bands at 3550(broad), 3110(w), 3070(w), 3020(w), 2995(s), 2950(m), 2910(m), 2860(m); 2770(w), 1725(vs), 1670(w), 1605(w), 1580(w), 1500(m), 1450(s), 1385(s), 1245(s), 1200(s), 1105(vs), 1025(s), 960(m), 890(w), 960(m), 760(s), and 695(s) cm^{-1} .

Analysis: Calculated for $\text{C}_{15}\text{H}_{18}\text{O}_3$: C, 73.12; H, 7.37. Found: C, 71.10; H, 7.06.

Thermal Polymerization of 2-Phenylallyl-2'-carboethoxyallyl Ether (V)

While attempting to distill a sample of the above monomer at full pump vacuum, it suddenly underwent spontaneous thermal polymerization. The polymer was surprisingly found to be completely soluble in

methylene chloride. The polymer was precipitated with methanol. The intrinsic viscosity in benzene at 30°C was 0.390 dl/g.

The IR spectrum (KBr) of the polymer gave absorption bands at 3480(broad) 3110(w), 3070(w), 3020(w), 2995(s), 2950(m), 2910(m), 2860(m), 2770(w), 1725(vs), 1670(w), 1605(w), 1580(w), 1500(m), 1450(s), 1385(s), 1245(s), 1200(s), 1105(vs), 1025(s), 960(m), 890(w), 860(m), 760(s), and 695(s) cm^{-1} .

Analysis: Calculated for $\text{C}_{15}\text{H}_{18}\text{O}_3$: C, 73.12; H, 7.37. Found: C, 71.14; H, 7.08.

Polymerization of 2-Phenylallyl Ether (X)

Charged to a polymer tube was 5.20 g (0.028 mole) of 2-phenylallyl ether, 4.40 g benzene, and 50 mg AIBN. The monomer solution was degassed by the freeze-thaw method at full pump vacuum and sealed. The polymer tube was then placed in a bath at 50°C. After 21 hr the polymer solution was precipitated with excess methanol to give 0.241 g (4.8%) of a white polymer. The intrinsic viscosity in benzene at 30°C was 0.125 dl/g.

The IR spectrum (KBr) gave absorption bands at 3100(w), 3070(m), 3040(m), 2940(m), 2860(m), 1604(m), 1585(w), 1500(m), 1475(w), 1450(m), 1240(w), 1100(s), 760(m) and 690(s) cm^{-1} .

Analysis: Calculated for $\text{C}_{18}\text{H}_{18}\text{O}$: C, 86.35; H, 7.25. Found: C, 85.49; H, 7.39.

Polymerization of 2-Phenylallyl Ether (X) with Boron Trifluoride

A 100-ml, three-necked, round-bottomed flask was equipped with a drying tube, magnetic stirring bar, nitrogen inlet, and boron trifluoride bubbler. The dried apparatus was cooled in a Dry Ice-ethanol bath. Charged to the flask was 40 ml methylene chloride, 10 ml chloroform, and 2 ml 2-phenylallyl ether. Boron trifluoride was added to the cold solution at a slow rate for 1-1/2 min. The bath was charged with Dry Ice and left overnight.

The next morning the reddish solution was poured into excess methanol, giving a pink polymer. The polymer was dissolved in dimethylformamide and reprecipitated in methanol. The intrinsic viscosity of the polymer in benzene at 30°C was 0.070.

The IR spectrum (KBr) of the polymer gave absorption bands at 3440(broad), 3100(w), 3070(w), 3040(w), 2940(w), 2870(w), 1608(m), 1500(m), 1450(m), 1080(s), 755(s), and 700(s) cm^{-1} .

Analysis: Calculated for $\text{C}_{18}\text{H}_{18}\text{O}$: C, 86.35; H, 7.25. Found: C, 86.16; H, 7.20.

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