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Copolymers of 1,4-Dienes with Monoolefins via a Cyclocopolymerization Mechanism

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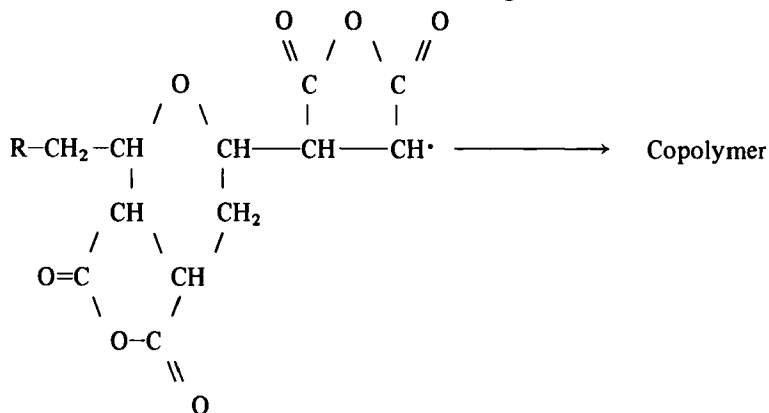
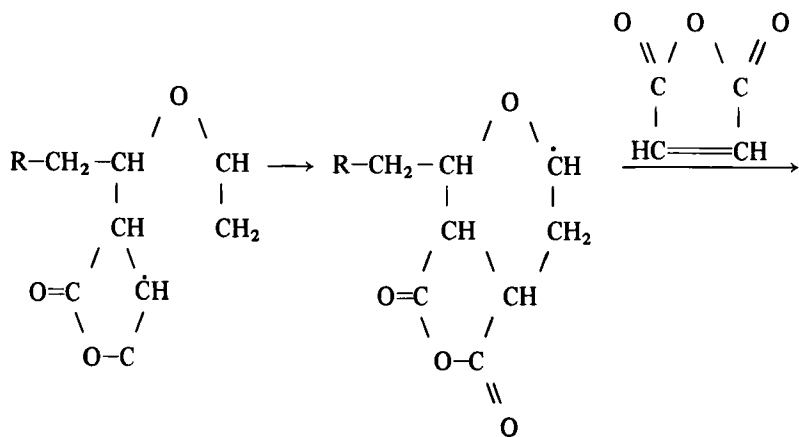
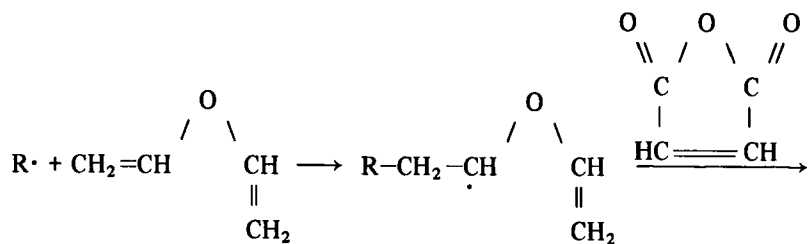
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SUMMARY

The copolymerizations of divinyl ether, divinyl sulfone, and 1,4-pentadiene with certain monoolefinic monomers were studied. High molecular weight (inherent viscosity > 1.0) copolymers of divinyl ether with maleic anhydride could be prepared using dichlorobenzoyl peroxide as the initiator. Derivatives of this copolymer were also prepared and studied. Divinyl sulfone and 1,4-pentadiene also gave soluble polymers with maleic anhydride but the inherent viscosities were much lower. Copolymerizations of these three dienes with dimethyl maleate, acrylonitrile, or vinyl acetate gave either low molecular weight materials at low conversions or cross-linked polymer at higher conversion. All of the soluble copolymers obtained showed little aliphatic unsaturation in the infrared, supporting the cyclocopolymerization theory.

INTRODUCTION

It has been previously observed by Butler [1, 2] that certain 1,4-dienes are capable of copolymerizing with monoolefins by a bimolecular alternating inter-intramolecular mechanism. These copolymers possess a repeat unit



which contains a cyclic unit alternating with a monoolefin unit. The mechanism is illustrated using divinyl ether and maleic anhydride as the comonomers.

Previous investigations of this type of copolymerization have been reported using divinyl ether, divinyl sulfone, divinyl dimethyl silane, 1,4-pentadiene, 3,3-dimethyl-1,4-pentadiene, and *N,N*-divinyl aniline as the diene with various olefinic compounds [4-7]. Reactivity ratio data have been generated for many of the comonomer pairs and a general copolymer composition equation has been developed [4-6]. No high molecular weight copolymers have as yet been reported in the cyclocopolymerization studies. The inherent viscosities of the copolymers obtained have usually been in the range of 0.05 to 0.25 and the conversions obtained have been kept low to avoid cross-linking.

The present study involves the copolymerization of several 1,4 dienes with monoolefins in attempts to prepare high molecular weight materials in good yields.

RESULTS AND DISCUSSION

Divinyl Ether Copolymers

The results of the copolymerizations of divinyl ether are summarized in Table 1.

The copolymers of divinyl ether with maleic anhydride obtained in this study were found to have much higher inherent viscosities than any such copolymer yet reported. The copolymers analyze as 2:1 maleic anhydride-divinyl ether copolymers and show little aliphatic unsaturation in the IR spectra. The copolymers are soluble in concentrated H_2SO_4 and dimethyl formamide and dissolve with reaction in dilute aqueous alkali, methanol, and ethanol. Inherent viscosities of 1.7 have been obtained for DMF solutions of these copolymers. Concentrated solutions prepared in DMF have been extruded into water-DMF solutions from a hypodermic syringe to give brittle fibers and cast on glass plates to give brittle films.

Solutions could be prepared in 97% H_2SO_4 which showed no viscosity change on standing at room temperature for 5 days. The copolymer could be recovered from this solvent apparently unchanged.

These copolymers do not melt but soften at about $230^\circ C$ and begin to decompose at $290-300^\circ C$.

Several derivatives of this copolymer were prepared and characterized.

Table 1. Copolymers of Divinyl Ether^a

M ₂ Comonomer	Solvent	Monomer conc (m/l)	Initiator ^β (wt. % based on monomer)	Conversion (%)	[η] inh	Mole fraction M ₂ (polymer)
Maleic anhydride	Benzene	3.3	DCBP - 0.5%	87	0.55b	0.67e
"	"	1.6	DCBP - 0.25%	80	0.612b	0.66
"	"	3.3	DCBP - 0.25%	84	1.002b	0.66
"	"	1.32	DCBP - 0.25%	55	1.31b	0.68
"	"	1.32	DCBP - 0.25%	53	1.69c	0.67
Dimethyl maleate	Benzene	1.32	DCBP - 0.5%	8	—	0.69
"	H ₂ O	3.3	K ₂ S ₂ O ₈ - 1%	93	Insol	0.63
"	"	3	NaHSO ₃ - 1%	70	Insol	0.65
"	"	2.6	Na ₂ S ₂ O ₄ - 0.1%	60	0.802d	0.65
"	"	2.6	NaHSO ₃ - 0.2%			
"	"		Na ₂ S ₂ O ₄ - 0.6%			
"	"		NaHSO ₃ - 0.6%			

Acrylonitrile	Benzene	1.1	DCBP - 0.5%	10	Insol	0.75
"	H ₂ O	1.32	K ₂ S ₂ O ₈ - 1.3% NaHSO ₃ - 1.3%	15	Insol	0.72
"	Benzene	1.3	DCBP - 0.5%	18	Insol	0.74
Vinyl acetate	Benzene	4.0	DCBP - 0.5%	3 (grease)	—	0.80
"	H ₂ O	3.3	K ₂ S ₂ O ₈ - 0.4% NaHSO ₃ - 0.4%	0	—	—

^aCharge ratio 1 mole divinyl ether to 2 moles M₂.

^b0.4 g/100 ml in H₂SO₄ (97%).

^c0.4 g/100 ml DMF.

^d0.4 g/100 ml HMPA.

^eCalculated from elemental analysis.

^fCharge ratio 1 mole divinyl ether to 4 moles dimethyl maleate.

gDCBP = dichlorobenzoyl peroxide.

Treatment of a copolymer, having an inherent viscosity of 1.31 in 97% H_2SO_4 , with hot water gave a polyacid which was soluble in water and ethanol. The polyacid had an inherent viscosity of 1.51 in ethanol and 1.76 in water. Brittle films and fibers could be obtained from concentrated solutions in ethanol. This derivative does not melt but begins to decompose at 290-300°C.

Half-ester copolymers were prepared by reaction of the copolyanhydride with ethanol or methanol. Both of these derivatives melt with decomposition between 285 and 300°C and give clear, brittle films and fibers from concentrated solutions. Elemental analyses and IR spectra indicate that these derivatives contain two ester and two acid groups per repeat unit.

Treatment of the copolyanhydride with *t*-butyl amine gave a product which analyzed for one amide and three acid groups per repeat unit. This amide-acid was soluble in DMF, DMSO, and formic acid. The derivative on heating to 135-150°C changes from white to a deep red color. Continued heating to 210°C results in decomposition as evidenced by gas evolution and a loss of color.

Copolymers of divinyl ether with dimethyl maleate, vinyl acetate, and acrylonitrile were also prepared. All of the copolymers prepared using acrylonitrile were insoluble, while only low yields of greases were obtained using vinyl acetate. The yields of copolymer obtained with each of these comonomers were low, varying from 3-8% for vinyl acetate to 8-18% for acrylonitrile. Both solution and emulsion polymerization systems were utilized. In the solution systems concentrations of divinyl ether were about 1 mole per liter.

Copolymers of divinyl ether and dimethyl maleate were also prepared in both solution and emulsion systems. The largest conversions were found to occur in an emulsion system using a persulfate-metabisulfite initiator system. If the conversion to copolymer was higher than 60%, the recovered copolymer was found to be insoluble. At conversions of 60% or less the copolymer was soluble only in hexamethyl phosphoramide. Inherent viscosities as high as 0.80 were obtained in HMPA. Insolubility in the more common solvents suggests that this copolymer is not entirely linear but is somewhat branched. IR spectra of these copolymers show somewhat more aliphatic unsaturation than do the divinyl ether-maleic anhydride copolymers, suggesting the opportunity for branching or cross-linking through these pendant vinyl groups.

Divinyl Sulfone Copolymers

The copolymerization of divinyl sulfone with monoolefinic monomers are listed in Table 2.

High molecular weight copolymers of divinyl sulfone with maleic anhydride could not be prepared. The highest inherent viscosity that could be obtained with this system was 0.13. Attempts to prepare higher molecular weight materials gave rise to insoluble, apparently cross-linked copolymer. The soluble copolymers obtained were shown by C, H, and S analyses to be 2:1 maleic anhydride-divinyl sulfone copolymers. Aliphatic unsaturation is present only in a low concentration as indicated by IR spectra.

One possible explanation for the inability to form high molecular weight copolymers of maleic anhydride with divinyl sulfone lies with the steric factors involved in the formation of the cyclic repeat unit. Space filling molecular models of the 2:1 maleic anhydride-divinyl ether repeat unit can be constructed with very little difficulty. Similar models of the maleic anhydride-divinyl sulfone copolymer show crowding of the second maleic anhydride unit. The larger size of the sulfone group also may retard the ring closure step giving rise to more pendant vinyl groups and thereby branching and cross-linking.

Other copolymers of divinyl sulfone were prepared using acrylonitrile, vinyl acetate, and dimethyl maleate as the comonomers. No high conversions to soluble copolymers could be obtained with any of these systems. At low conversions, however, soluble copolymers could be obtained when acrylonitrile or vinyl acetate were used. At a 13% conversion a 2:1 vinyl acetate-divinyl sulfone copolymer was obtained which had an inherent viscosity of 0.21 in DMF. The copolymer analyzed as 2.2:1 vinyl acetate to divinyl sulfone and showed little aliphatic unsaturation in the IR spectra. This material was soluble in DMF and DMSO and melted at 290-300°C with decomposition. Likewise a 7% conversion to soluble copolymer was obtained using acrylonitrile as the comonomer. The copolymer analyzed as a 3.0:1 acrylonitrile-divinyl sulfone copolymer and showed only little aliphatic unsaturation in the IR spectrum. The copolymer was soluble in DMF and had an inherent viscosity of 0.29 in this solvent. Upon heating to 230-250°C the copolymer began to darken in color. Attempts to prepare copolymers of divinyl sulfone with dimethyl maleate gave only products that were insoluble in all the solvents tested.

As pointed out above, steric considerations may prevent the formation of high molecular weight copolymers of divinyl sulfone with bulky comonomers. In this respect it is interesting that higher molecular weight

Table 2. Copolymers of Divinyl Sulfone^a

Comonomer M ₂	Solvent	Monomer conc (m/l)	Initiator d		Conversion (%)	[η] in h	Mole fraction M ₂ (polymer) ^c
			(wt. % based on monomer)				
Maleic anhydride	Benzene	2.4	BP - 2.5%		32	0.13 b	0.66
"	DMF	2.4	BP - 2.5%		0	—	—
"	Benzene	2.4	AIBN - 2.5%		26	0.13 b	0.68
"	"	2.4	BP - 1.25%		23	0.07 b	0.67
"	"	2.4	BP - 0.625%		12	0.04 b	0.67
"	"	0.94	DCBP - 2.5%		27	0.13 b	0.65
Dimethyl maleate	H ₂ O	0.94	K ₂ S ₂ O ₈		15	Insol	0.60
"	"	0.94	NaHSO ₃ - 2.0%		10	Insol	0.63
"	"		K ₂ S ₂ O ₈ - 1.0%				
"	"		NaHSO ₃ - 1.0%				

Acrylonitrile							
"	Benzene	2.4	BP - 2.5%	35	Insol	0.72	
"	"	1.0	DCBP - 0.5%	6	—	—	
"	"	1.0	DCBP - 1.0%	6.5	0.29b	0.75	
		2.0	DCBP - 1.0%	8	0.21	0.73	
Vinyl acetate	Benzene	4.0	BP	4.5	Insol	0.70	
"	H ₂ O	1.5	K ₂ S ₂ O ₈	70	Insol	0.68	
"			NaHSO ₃ - 2.5%				
"	Benzene	0.94	DCBP - 1.25%	13	0.21b	0.69	
"	"	0.94	DCBP - 1.25%	9.0	0.19b	0.71	

a Charge ratio 1 mole divinyl sulfone to 2 moles M₂.

b 0.4 g/100 ml in DMF.

c Calculated from elemental analyses.

d BP = benzoyl peroxide. AIBN = Azobisisobutyronitrile. DCBP = Dichlorobenzoyl peroxide.

Table 3. Copolymers of 1,4-Pentadiene^a

Comonomer M ₂	Solvent	Monomer concn (m/l)	Initiator (wt. % based on monomer)	Conversion (%)	[η] in ^b	Mole fraction ^c M ₂ (polymer)
Maleic anhydride	Benzene	2.0	DCBP	7	—	—
"	Xylene	1.5	BP - 175%	55	0.25 ^b	0.67
"	"	2.5	BP - 0.7%	48	0.29 ^b	0.68
Vinyl acetate	H ₂ O	1.5	K ₂ S ₂ O ₈ - 2% NaHSO ₃ - 2%	Trace - grease	—	—
"	Xylene	2.5	BP - 1.75%	Trace - grease	—	—

^aCharge ratio 1 mole 1,4-pentadiene to 2 moles M₂.

^b0.4 g/100 ml DMF.

^cCalculated from elemental analyses.

copolymers were obtained with vinyl acetate and with acrylonitrile than could be prepared with maleic anhydride. The space filling model of the vinyl acetate copolymer is much less crowded than that of maleic anhydride, and the acrylonitrile copolymer model is the least crowded. These observations are in agreement with the inherent viscosities of the copolymers obtained. The acrylonitrile copolymer has the highest inherent viscosity.

1,4-Pentadiene Copolymers

Table 3 contains a summary of the results of copolymerization involving 1,4-pentadiene.

Copolymers of 1,4-pentadiene and maleic anhydride were prepared in 50% conversion and with inherent viscosities as high as 0.29 in DMF. Analyses indicate that this composition is 2:1 maleic anhydride-1,4-pentadiene and the IR spectra indicates little aliphatic unsaturation. Brittle films could be obtained from DMF solutions of this copolymer. The copolymer began to soften at 118°C, decomposition without darkening began at 250°C, and noticeable discoloration started at 310°C.

The observations as to conversion and inherent viscosity are in agreement with those made above regarding the steric requirements of the divinyl ether and divinyl sulfone copolymers with maleic anhydride. The methylene group present in 1,4-pentadiene is smaller than the sulfone group but larger than the oxygen ether. Thus on this basis there is a trend toward higher inherent viscosity and conversion with decreasing size in the central group of the diene. Obviously other factors are affecting the molecular weight of the copolymers obtained. Among these are chain transfer of the divinyl sulfone and degradative chain transfer in the case of 1,4-pentadiene. Further experimentation is necessary to assess these factors.

Attempts to prepare copolymers of 1,4-pentadiene with vinyl acetate in solution and in emulsion systems lead to, at most, trace amounts of greasy materials. These greases probably were low molecular weight polyvinyl acetate as the result of degradative chain transfer.

EXPERIMENTAL

Materials

All of the monomers and solvents used in this study are commercially available. The monomers were purified by suitable means prior to use.

Polymerizations

Solution Polymerizations. The monomers and initiators were weighed out and placed in a three-necked flask along with the solvent. The solution was heated, by means of an oil bath, and stirred under a nitrogen atmosphere for a given period. Depending on the solvent and monomers used, the copolymer was recovered by direct filtration or by precipitation in a nonsolvent, followed by filtration. The copolymer was washed thoroughly and dried in a vacuum oven. The per cent conversion is based on the weight of copolymer obtained. In the case of 1,4-pentadiene copolymerization, a pressure bottle was used instead of the reaction flask. The bottle was swept with nitrogen before sealing.

Emulsion Polymerization. The monomers were weighed and added to a known volume of water containing 0.5% sodium lauryl sulfonate. The mixture was stirred and sodium metabisulfite and potassium persulfate added separately as aqueous solutions. A nitrogen atmosphere was maintained throughout the polymerization. The copolymer emulsion was coagulated by the addition of a saturated NaCl solution. The copolymer was filtered, washed thoroughly with water, and dried in a vacuum oven.

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