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Allylic Polymers. Diallyl 2-Substituted Succinate Prepolymers and Their Properties

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Synopsis

Diallyl 2-substituted succinates, obtainable via the addition of alkenes or alkylaromatics to maleic anhydride, undergo intramolecular cyclization during polymerization to low molecular weight prepolymers. The amount of this cyclization and the properties of the cured prepolymers are profoundly affected by the structure of these 2-substituents. Thus, the degree of cyclization decreases with these substituents in the order: aralkyl and isobutyl > unhindered alkenyl > alkyl > hindered alkenyl. Properties of thermosetting molding compounds based on these prepolymers are inferior to those of poly(diallyl phthalate) molding compounds.

INTRODUCTION

The facile alkylation of maleic anhydride with olefins and alkylaromatic compounds offers a route to a series of moderately priced monomers. Thus, a variety of diallylic succinates are available by the alkyl esterification of these alkylsuccinic anhydrides. This paper reports on prototypes of this diallyl series relative to their polymerization characteristics, curing characteristics, and comparative properties of their prepolymers with similar commercial thermosetting materials.

The diallyl succinates investigated were derived from the addition products of maleic anhydride with toluene, ethylbenzene, cumene, tripropylene, tetrapropylene and its hydrogenated derivative, diisobutylene, and isobutylene.

Alkenes and alkylaromatic compounds readily form 2-substituted products with maleic anhydride at elevated temperatures by addition of the allylic or benzylic C—H grouping across the carbon–carbon double bond of the maleic anhydride. For example, propene[1] and alkylaromatic hydrocarbons[2–4] such as toluene, add in the manner shown in eqs. (1) and (2).

Since this process was first patented,[5] a large number of other patents and publications, relating to the addition of monoolefins to maleic anhydride have issued,[6–23] including isobutylene,[1,9,19] diisobutylene,[9,18] tripropylene,[21,24] and tetrapropylene.[13,21]

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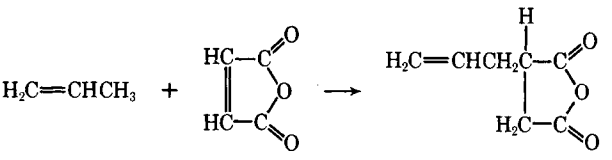

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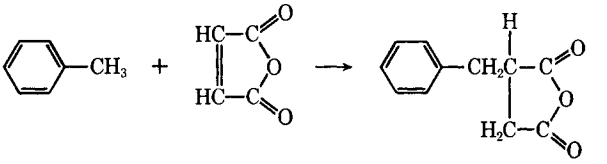

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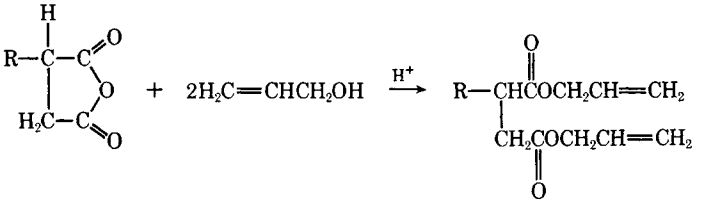
Related patents disclose the formation of alkylsuccinic acids[25] and dialkyl alkylsuccinates[23] by the hydrogenation of the corresponding C-alkenyl derivatives.

Armitage et al.[11] described polymerizable diallyl (or dimethallyl) alkenylsuccinates which are prepared by the esterification of the corresponding alkenylsuccinic anhydrides with allyl alcohol:



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Such esters are said to be suited for use in surface coatings.

EXPERIMENTAL

Preparation of 2-Substituted Succinic Anhydrides

The following 2-substituted succinic anhydrides from Humphrey-Wilkinson, Inc., were purified by vacuum distillation prior to esterification or hydrogenation: diisobutenyl (150°C/0.8 mm); nonenyl or tripropylene (178°C/0.4 mm); and dodecenyl or tetrapropylene (160–162°C/0.2 mm).

The other 2-substituted succinic anhydrides were prepared[26] by the addition of monoolefins or alkylbenzenes to maleic anhydride in benzene or excess of the alkylbenzenes (when they were the alkylation agents) in an autoclave in the temperature range of 180–200°C and 600–1000 psig pressure. Peroxide initiators were employed with the alkylbenzenes while pyrogallol was used as an inhibitor in the alkenylation reactions. The alkylsuccinic anhydrides were prepared[26] by the hydrogenation of the corresponding alkenylsuccinic anhydrides using a Pd/C catalyst in methylcyclohexane solvent with the use of hydrogen pressures of 300–900 psig and temperatures of 120–130°C. The distilled liquid adducts had the following boiling points: isobutyl (160°C/28 mm) and dodecyl (182–184°C/1.1 mm). The distilled solid adducts had the following melting points:

benzyl (159–160°C); 1-phenethyl (145–146°C); and 1-methyl-1-phenethyl (128–130°C).

Preparation of Diallyl 2-Substituted Succinates

Esterification of the 2-substituted succinic anhydrides with allyl alcohol in benzene at 85°C with *p*-toluenesulfonic acid as catalyst and a Dean-Stark water separator yielded the diallyl alkylsuccinates, diallyl alkenylsuccinates, and diallyl benzylsuccinates[26] which had the following boiling points: 1-methyl-1-phenethyl (142°C/0.08 mm); 1-phenethyl (176°C/0.1 mm); benzyl (175–178°C/0.5 mm); isobutyl (124–126°C/0.1 mm); dodecyl (160°C/0.3 mm); diisobutenyl (145°C/0.26 mm); nonenyl (160°C/0.25 mm); and dodecenyl (158–161°C/0.13 mm).

Polymerization of the Diallyl Succinates

G. E. Gel Times and Gel Point Conversions. Comparative rates of polymerization for the diallyl 2-substituted succinate monomers were obtained by determining their G. E. gel time[27] (see Table I). This was determined by the standard procedure of heating the monomer containing 1 wt-% benzoyl peroxide at 100°C and recording the time to incipient gelation.

The conversion at the gel point was determined in the following manner. A weighed sample of the monomer containing 1–2 wt-% of an initiator, e.g.,

TABLE I
Comparative Rates of Polymerization and Gel Point Conversions of Diallyl 2-Substituted Succinates

	G.E. gel time, (at 100°C), min[a]	Gel point conversion (at 130°C), %[b]
2-Substituted diallyl succinates		
1-Methyl-1-phenethyl	320[c]	34
1-Phenethyl	101	37
Benzyl	123	33
Isobutyl	63	32
Dodecyl	>420	48
Diisobutenyl	>480	44
Nonenyl	>400	35
Dodecenyl	>120	42–45
Other diallylic monomers		
Diallyl phthalate	41	25
Diallyl isophthalate	26.5	25
Diallyl maleate	4	17[d]

[a] Times significantly beyond 120 min have little meaning since the initiator has been consumed by then.

[b] Precision: ±2%.

[c] A duplicate sample did not gel in 343 min.

[d] Determined at 125°C.

tert-butyl perbenzoate or benzoyl peroxide, in a test tube was heated in a constant temperature bath maintained at 130°C. At the point just before incipient gelation (as detected by a precipitous increase in viscosity) the samples were instantaneously chilled to inhibit further polymerization. The prepolymer was precipitated by pouring the monomer–polymer solution into methanol. It was further purified by reprecipitation which consisted of redissolution in acetone or benzene and precipitation into methanol. Conversion at the gel point was determined from the weight of the recovered polymer after it was freed of solvents. These values are also recorded in Table I.

Preparation of Prepolymers. Prepolymers of the diallyl 2-substituted succinates were prepared by mass polymerizations performed in the resin flask fitted with a stirrer, water condenser, thermometer, and nitrogen inlet to maintain an inert atmosphere. All polymerizations were performed at 130°C except that of diallyl 2-(1-phenethyl)succinate which was conducted at 100°C. The reaction conditions and conversions are recorded in Table II. The amounts of initiator required to produce reasonable polymerization rates were estimated on the basis of the G. E. gel times. The polymerizations were normally terminated well short of the gel point.

In general, the prepolymers were difficult to precipitate in a tackfree, dispersed form from methanol. Therefore, all the crude prepolymers were

TABLE II
Bulk Polymerization of Diallyl Succinates at 130°C

	Initiator		Reaction time, hr	Conversion, %
	Compound[a]	Wt-%		
2-Substituted diallyl succinates				
1-Methyl-1-phenethyl	BP	1.0	1.0	28
	TBP	0.25	2.5	23
1-Phenethyl	TBP	0.1	7.5	21
	TBP	0.1	16.5	24
Benzyl	TBP[b]	0.2	9.0	29
Isobutyl	TBP	[c]	7.0	21
Dodecyl	TBP	0.5	6.5	26
Diisobutenyl	TBP	1.0	2.0	37
Nonenyl	TBP	1.0	3.5	16
Dodecenyl	TBP	1.0	2.5	18
Other diallyl monomers				
Diallyl phthalate	TBP	0.25	1.0	25[d]
Diallyl isophthalate	TBP	0.15	1.1	25

[a] TBP = *tert*-butyl perbenzoate; BP = benzoyl peroxide.

[b] Added incrementally: 0.1 wt-% initially and 0.1 wt-% when dope viscosity reached 0.75 P.

[c] The initial charge was taken to 1.5 P with 0.6 % TBP added incrementally. It gelled upon addition of another 0.1% TBP.

[d] Reaction temperature 125°C.

TABLE III
Physical Properties of Diallyl Succinate Prepolymers and Dapon

	$\bar{M}_n$[a]	Melting range, °C	Iodine number		Number of C=C groups/repeat unit		Pendant allyl groups cyclized, %
			Calcd	Found[b]	Theoretical	Actual[c]	
2-substituted diallyl succinates							
1-Methyl-1-phenethyl	4020	84–90 97–105	80	47[d] 46	1	0.59	41
1-Phenethyl	—	55–75	84	54–57	1	0.66	34
Benzyl	—	45–65	88	54[d]	1	0.61	39
Isobutyl	—	—	100	63[d]	1	0.63	37
Dodecyl	—	60–65	69	54[d]	1	0.78	22
Diisobutenyl	3710	46–54	164	150	2	1.83	17[e]
Nonenyl	6920	40–55	157	117	2	1.49	51[e]
Dodecenyl	9520	50–60	139	110	2	1.56	44[e]
H[f]	4050	—	—	—	1	0.74	26
Other prepolymers							
Dapon 35	15,000[g]	80–100	102	57	1	0.56	44
Dapon M	10,000	75–84	102	80–84	1	0.84	16

[a] Number-average molecular weight (determined by cryoscopy).
[b] Strain method (saponification followed by titration with bromide-bromate).
[c] Based on iodine number.
[d] Wijs method.
[e] Based on the arbitrary assumption that the 2-alkenyl substituents do not participate in cyclization (see Discussion).
[f] Data of Holt and Simpson.[80]
[g] Determined by osmometry.

reprecipitated from acetone or benzene solutions into cold methanol. Number average molecular weights, $\bar{M}_n$, were determined cryoscopically using benzene solutions. These $\bar{M}_n$ values, melting ranges, and unsaturation (iodine numbers) of the prepolymers are presented in Table III. Iodine numbers were determined by two procedures: (*1*) the method of Wijs and (*2*) the method of Strain.[28] The Strain method is considered to be more reliable for saponifiable polymers.

Cured Polymers

Castings with Monomers. Attempts to make cast specimens from diallyl (diisobutenyl)succinate with 2 wt-% *tert*-butyl perbenzoate were unsuccessful due to the onset of strain patterns leading to severe cracking even though the specimens were undercured.

Molded Prepolymers. The prepolymers were evaluated as molding resins in both filled and unfilled formulations. Test specimens (5 × 1/2 × 1/8 in.) from the former were prepared in a transfer molding press while

TABLE IV

Ingredient	Content, parts		
	Formulation 1	Formulation 2	Formulation 3
Prepolymer	100	100	100
tert-Butyl perbenzoate	3	3–5	4
Duramite	75	60	—
Asbestos[a]	—	15	20
TiCal[b]	70	70	40
HiSil[c]	10	10	20
Lauric acid	2	2	2
Pigment	2	2	3

[a] Arizona white asbestos, 1/2 in. fiber length.
[b] TiO_2–$CaSO_4$ (DuPont).
[c] SiO_2 (Columbia Southern).

specimens from the latter were made in a compression molding press. The molding pressure was 8000 psi. Curing times were 30 min in compression molding at 150, 160, or 170°C. On the other hand, all transfer molding was done at 150°C with curing times of 15, 30, and 60 min.

The unfilled prepolymers which were used in compression molding were blended with 3 wt-% of *tert*-butyl perbenzoate prior to molding.

Filled compositions used in transfer molding contained mineral fillers alone or in combination with a reinforcing filler, viz., asbestos fibers. These formulations are listed in Table IV.

Properties of the cured polymers compositions are given in Table V and VI.

TABLE V
Properties of Cured, Unfilled Diallyl Succinate Prepolymers Compression-Molded at 8000 psi for 30 min[a]

	Molding temp, °C	Flexural properties			Rockwell hardness (M)	HDT, °C[b]
		Strength, psi	Modulus, psi × 10^{-6}	Elongation, %		
2-Substituted diallyl succinates						
1-Methyl-1-phenethyl	170	4830	0.32	1.6	—	86
	160	5440	0.32	1.8	—	91
1-Phenethyl	160	5540	0.36	1.6	83	78
	150	3390	0.34	1.0	86	95
Benzyl	160	4650	0.40	1.2	—	100
Isobutyl	150	3610	0.27	1.4	Shattered	93
Dodecyl	150	3700	0.16	2.6	—	50
Diisobutenyl	170	4900	0.26	2.0	Bars	76
	150	4770	0.26	1.9	Shattered	80
Nonenyl	150	Did not cure	—	—	—	—
Dodecenyl	170	Did not cure	—	—	—	—
Other prepolymers						
Dapon 35	150–160	9000	0.5	1.6	114–116	155
Dapon M	150–160	8300	0.5	—	119–121	>245[c]

[a] With use of 3 wt-% *tert*-butyl perbenzoate.
[b] Heat distortion temperature; determined at 264 psi fiber stress.
[c] Broke at 6 mil deflection. HDT at 564 psi fiber stress = 186°C.

TABLE VI
Properties of Cured, Filled Diallyl Succinate Prepolymers Transfer-Molded at 150°C[a]

	Molding time, min	Formulation: No. (Table IV)	Formulation: Reinforcing filler present[b]	Flexural properties: Strength, psi	Flexural properties: Modulus psi × 10^{-6}	Flexural properties: Elongation, %	HDT, °C[c]
2-Substituted diallyl succinate							
1-Methyl-1-phenethyl	15	3	Yes	2280	0.61	0.49	79
	60	2[d]	Yes	3790	0.68	0.63	79
1-Phenethyl	30	1[e]	No	3070	0.64	0.54	69
	30	2[e]	Yes	4370	0.82	0.64	84
Benzyl	15	1[d]	No	—	—	—	69
	30	1[d]	No	2720[f]	0.61	0.74[g]	81
Other prepolymers							
Dapon 35	15	1[d]	No	7000–9000	0.6		155
	15	2[d]	Yes	9600	1.2		232
Dapon M	15	1[d]	No	13000	0.55		260
	15	2[d]	Yes	13000	1.2		260

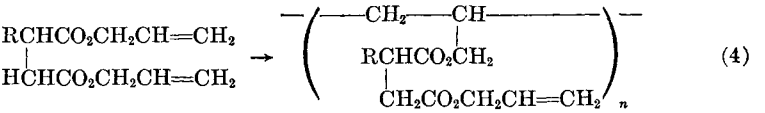
[a] With and without asbestos reinforcing fibers. The complete formulation is listed in Table IV.
[b] Asbestos fiber, 20 parts.
[c] At 264 psi fiber stress.
[d] 3 or 4 parts TBP.
[e] 5 parts TBP.
[f] Bad scatter: 935–5540 psi.
[g] A number of bars cracked during molding.

DISCUSSION

Diallylic monomers polymerize in two steps to produce thermosetting resins. The first step encompasses that phase of the polymerization which takes place before gelation occurs. This produces a soluble, fusible β-polymer (or prepolymer) which may be pictured as a substituted polyethylene whose pendant groups contain the allyl moiety. The second phase of the polymerization begins with incipient gelation in the polymerization reaction or during the curing (molding) of the prepolymer. It involves crosslinking of the β-polymer through the pendant allyl groups and yields a γ-polymer or thermoset resin.

Polymerization Characteristics of Diallyl Succinates

Diallyl succinates, analogously to diallyl *o*-phthalate (DAP) and diallyl isophthalate (DAIP), homopolymerize to form prepolymers below the gel point according to eq. (4).



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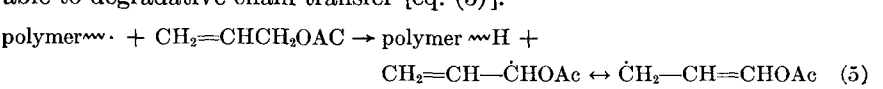
All of the diallyl succinate monomers tested in this study polymerized at a much lower rate than that observed for either DAP or DAIP. This is shown by the G. E. gel time data (Table I) and is manifested not only in the polymerization reaction itself but also during curing of the prepolymers. These data also show that the gel point conversions of these prepolymers are all higher than that of either Dapon 35 or Dapon M (tradenames of the propolymers of DAP and DAIP, respectively).

Conditions for the preparation of the diallyl succinate prepolymers by bulk polymerization are shown in Table II. A comparison of rates of polymerization with those of DAP and DAIP shows these latter to have much higher rates of polymerization in concordance with the G. E. gel time data.

Diallylic monomers, particularly the diallyl phthalates, have significantly better polymerization characteristics than do the monoallylic monomers which polymerize sluggishly, require large amounts of initiator and form only oligomers. For example, Bartlett and Altschul[29] found that the rate of polymerization of allyl acetate was abnormally low and that the degree of polymerization was independent of initiator concentration. This is ascribable to degradative chain transfer [eq. (5)].



(5)

These resonating allyl radicals terminate by dimerizing but occasionally may react with monomer to initiate a new polymer chain. This latter activity, effective chain transfer, becomes quite prevalent in DAP polymerization at the expense of degradative chain transfer. A demonstration

of this phenomenon is seen in the fact that under identical polymerization conditions the conversion to polymer of DAP is much higher than that of allyl acetate. For example, the yields are 86% and 12% respectively, with the use of 1 wt-% benzoyl peroxide initiator at 80°C.[30]

Characteristics of Diallylic Succinate Prepolymers

The physical properties of the prepolymers of the diallyl 2-substituted succinates are compared with those of Dapon 35 and Dapon M in Table III. The former, with the exception of the 1-methyl-1-phenethylsuccinate polymer, have lower melting points.

The comparative degrees of cyclization of these prepolymers, as derived from iodine numbers, follow a predictable trend. In order to understand this pattern a knowledge of the vagaries of the diallylic polymerization behavior is helpful.

Simpson[31] reported that the degree of unsaturation of the DAP prepolymer was about one-fourth that of the monomer. This means that about one-half of the pendant allyl groups of the β-polymer become saturated through incestuous polymerization (cyclization). This is an exceptional case, since it was found[31] that the normal amount of unsaturation remaining in other diallylic prepolymers was of the order of 40% of that of the monomer, i.e., only about 20% of the pendant allyl groups cyclized. By actual measurement Simpson found that in the DAP prepolymer about 46% of the pendant allyl groups were used in cyclization reactions. It will be noted that the value, 44%, found in the present work checks this closely (see Dapon data in Table III).

The amount of cyclization in DAP polymerization does not explain entirely the observed disparity between the experimental and the theoretical gel point observed in this system. Minnema and Staverman[32] have resolved similar discrepancies occurring in vinyl–divinyl copolymerizations, and their findings may apply to DAP polymers where shielding of pendant allyl groups begins to occur.

Table VII lists the per cent cyclization, degree of polymerization (DP) of the chains, and gel point conversions of a number of diallylic prepolymers as reported by Holt and Simpson.[30] It is interesting to note that of these monomers DAP undergoes the greatest amount of cyclization during polymerization with diallyl diphenate showing almost as much tendency to cyclize. This is explicable on the basis of the contiguity of the carballoxy groups in each monomer. As expected the per cent cyclization decreases for the diallylic phthalates in the order: *o*-phthalate > isophthalate > terephthalate.

In the aliphatic series the per cent cyclization was 20 ± 3% with the exception of diallyl succinate, for which the value was somewhat higher (26%). Superficially this appears to be an anomalous value since, on the basis of comparable geometrical structures, this monomer should have about the same tendency to cyclize as does DAP. However, it would be anticipated that the greater rigidity of the latter monomer would give it a

TABLE VII
Amount of Intramolecular Cyclization, Degree of Polymerization, and Gel Point Conversion of a Number of Diallylic Prepolymers

Diallyl diester	Pendant allyl groups cyclized, %[a]	Degree of polymerization of chains[b]	Gel point conversion, %
o-Phthalate	46	19.8	25
Isophthalate	16	19.8	25
Terephthalate	12	19.6	25
Diphenate	39	15.1	—
Carbonate	23	20.0	—
Oxalate	19	20.0	26
Malonate	19	20.0	—
Succinate	26	20.4	—
Glutarate	20	20.0	—
Adipate	21	19.3	—
Sebacate	18	19.4	—
Azelate	17	20.0	—

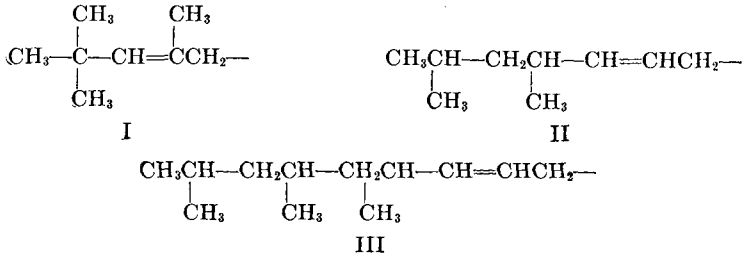
[a] Data of Holt and Simpson.[30]
[b] Number of double bonds reacted per linear chain.

relatively greater ability to cyclize. It is noteworthy that the degree of polymerization of the chains (number of double bonds reacted per chain) is the same (19–20) for all of these polymers except diallyl diphenate.

A comparison of the data on the prepolymers of diallyl succinate and diallyl 2-substituted succinates (last column, Table III) reveals that the nature of the 2-substituents has a profound effect on the degree of cyclization. The aralkyl substituents impart rigidity to the molecule and thereby enhance cyclization (37.5 ± 3.5%). This compares with a degree of cyclization of only 26% for the polymer of diallyl succinate itself. It appears that the α,α-dimethylbenzyl (or 1-methyl-1-phenethyl) group is the most effective in agreement with theory. In the alkyl series the bulky isobutyl group appears to be about equally efficacious in this respect as is shown by the 37% cyclization of the diallyl 2-isobutylsuccinate polymer. However, as the alkyl chain length increases it can retard cyclization to increasing extents through entanglement with the pendant allyl groups (shielding effect). This effect is demonstrated by the dodecyl group in diallyl 2-dodecylsuccinate and the diisobutenyl group in diallyl 2-diisobutenylsuccinate which cyclize only to the extent of 22% and 17%, respectively. Another facet must be considered when the 2-substituent is an alkenyl group which can also participate in cyclization. This would explain the high percentage of cyclization (51 and 44%) for the nonenyl and dodecenylsuccinate prepolymers. In accord with the entanglement hypothesis, the larger dodecenyl group leads to the smaller degree of cyclization (44% versus 51%).

A question immediately arises concerning the anomalously low degree of cyclization in the 2-diisobutenyl polymer as compared with that of either the nonenyl or dodecenyl polymers. The apparent disparity is explicable

on the basis of the much lower activity of the carbon–carbon double bond in the diisobutenyl group as compared to that of the nonenyl or dodecenyl groups. This is expected, since the former is a trisubstituted ethylene (I) and the latter two are disubstituted ethylenes (II and III).



It is well known that trisubstituted ethylenes are very reluctant to undergo radical-initiated polymerization.

The relative order of reactivity of these groups in comparison with the pendant allyl groups is: allyl > II or III > I. The fact that the diisobutenyl prepolymer has a lower degree of cyclization than the prepolymer of the unsubstituted diallyl succinate (17% compared to 26%) corroborates the fact that the diisobutenyl group participates to no significant degree in the cyclization reaction. It further indicates that this substituent partially inhibits the normal homocyclization of the pendant allyl groups. Therefore it is not surprising that the degree of cyclization is affected to about the same extent by this substituent and the completely unreactive dodecyl group (17% compared to 22% cyclization).

If one assumes that the reactivities of nonenyl and dodecenyl groups are comparable to that of the allyl group, then the polymer repeat unit can be considered to be comprised of two equally reactive pendant allyl groups. It is interesting to note that the per cent cyclization for the nonenyl and dodecenyl polymer then becomes 25.5% and 22%, respectively, which is in good agreement with the values for the 2-dodecyl polymers. Thus, assuming complete inactivity of the diisobutenyl group it can be seen that the degree of cyclization for the 2-dodecyl and 2-alkenyl substituted polymers is substantially the same as that of the unsubstituted diallyl succinate prepolymer.

Properties of Cured Prepolymers

The properties of the cured polymers are listed in Table V for compression-molded, unfilled specimens and in Table VI for transfer-molded, filled compounds. These data show that the diallyl succinate prepolymers as molding compounds are quite inferior to those of Dapon 35 and Dapon M. The former not only cure less readily but when cured are much less rigid, have much lower flexural strengths, have considerably lower hardness values, and have much lower heat distortion temperatures.

Since the prepolymers of the diallyl 2-aralkylsuccinates had the best balance of properties, further attempts were made to improve them by

formulating them with reinforcing fibers and fillers. Properties of transfer-molded compounds of such compositions (Table VI) indicate that (*1*) fillers neither enhance nor harm the properties, (*2*) asbestos fibers have only a slight reinforcing action, and (*3*) curing is not completed within a 15-min interval at 150°C. It should be noted that cure cycles of less than 2 min are normally prerequisites for commercial molding operations. As expected, the fillers increased the rigidity, but both the flexural strengths and the heat distortion temperatures (HDT) were thereby lowered.

CONCLUSIONS

Diallyl 2-substituted succinates polymerize more slowly than diallyl phthalates and their prepolymers cure slowly relative to diallyl phthalate prepolymers but they exhibit unusually high gel point conversions. The resulting prepolymers have low melting points, low molecular weights, and are generally somewhat difficult to recover from the polymerization mixture.

The degree to which these monomers cyclize during polymerization is profoundly affected by the structure of the 2-substituent. The per cent cyclization with these types was: 2-alkenyl, ca. 22%; 2-aralkyl and 2-isobutyl, ca. 37%; and long-chain 2-(*n*-alkyls), ca. 22%. The same general trend obtained for the mechanical and thermal (HDT) properties of these cured polymers with the 2-aralkyl polymers showing the best overall properties: flexural strength 5500 psi, flexural modulus 0.4×10^6 psi, Rockwell hardness M86, and HDT 100°C. Mineral fillers and fibers were inefficacious in improving these properties.

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