

Cross-linking of Amidated Polybutadiene with Resole. II.

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Synopsis

To prove the main cross-linking reaction between amidated polybutadiene and resole, cross-condensation reactions involving simple amide compounds and resole were examined. Amide compounds having both an amide group and a carboxylic acid group inhibited the self-condensation of resole itself. The cross-condensation products obtained from succinamic acid and 2-methylolphenol were separated using a preparative chromatography method to identify the cross-condensed products in which the main products were cross-condensed oligomers having an imide linkage. A cross-condensation scheme was proposed, and it was concluded that the main cross-linking reaction between amidated polybutadiene and resole also followed the same scheme.

INTRODUCTION

It was revealed¹ that amidated low-molecular-weight polybutadienes derived from maleinated polybutadiene and ammonia, reacting with resole under mild conditions, gave homogeneous cured resins. Based on the curing conditions, the effect of the succinamic acid functional group on the curing efficiency, and the behavior of the succinamic acid group on heating, it was concluded that cross-condensation between the succinamic acid group of amidated polybutadiene and the methylol group of resole was predominant in this system.

Cross-condensation reactions involving such functional groups have been studied using model compounds to elucidate the above scheme.

EXPERIMENTAL

Materials

2-Methylolphenol and various amide compounds were commercial reagents and used without further purification.

Condensation Between Amide Compounds and Resole

To the amide compound placed on an aluminum plate, 1 g of resole dissolved in acetone was added. The mixture was heated at 150°C for 1 h. The amide compound that reacted with resole gave a clear and homogeneous

resin; on the other hand, the amide compound that did not react resulted in incompatibility that was retained even after heating. In all runs, the weight loss was only 10 or 20% of the total amount of the materials charged, indicating that the amide compound had scarcely been evaporated in the procedure.

The resin obtained was crushed into small pieces that were extracted successively with a Soxhlet extractor in the following order: with hot acetone for 1 h to remove the unreacted resole fraction, with hot water for 2 h to remove the unreacted amide compound, and again with hot acetone for 1 h. The insoluble fraction was dried in vacuo.

Separation and Identification of Cross-Condensed Oligomers

Succinamic acid was reacted with 2-methylolphenol using the same procedure described above.

To identify the reaction products, the reaction mixture was at first separated by using a small-scale preparative gel-permeation chromatography method under the following conditions: column, polystyrene gel (10^2 – 10^2\AA), $22\text{ mm}\phi \times 60\text{ cm}$; solvent, chloroform, 8.6 mL/min; concentration, 5 wt%; temperature, 23°C ; detector, refractive index (RI). The oligomers separated were identified by infrared absorptiton spectrum, field diffusion mass spectrum, and ^{13}C -NMR spectrum. The composition of the oligomers was determined by the peak area of a gel-permeation chromatogram in which the RI sensitivity of each peak was measured by using the pure oligomers separated before quantitative analysis. The following conditions were used: column, polystyrene gel (G5000H6, G4000H6, G3000H8, and G2000H8); solvent, tetrahydrofuran, 1.5 mL/min; temperature, 23°C ; concentration, 2.5 wt%; detector, RI.

RESULTS AND DISCUSSION

Cross-condensation Between Amide Compounds and Resole

It is well known that amide compounds react with formaldehyde to give hydroxymethyl derivatives.^{2,3} Condensation reactions involving amide compounds, formaldehyde, and phenol have also been reported²; however, scarcely any detailed investigation has been made concerning cross-condensation reactions involving amide compounds and resole, since these reactions compete with the condensation reaction of resole itself, and it is complicated to identify reaction products. It seems that results on condensation reaction between resole and succinamic acid or phthalamic acid, both of which contain an amide group and a carboxylic acid group, has not been referred.

The experimental results in the former report¹ indicated that efficient cross-linking occurred between amidated polybutadiene and resole. The resole was presumed to react efficiently with the succinamic acid group in the amidated polybutadiene as well as with resole itself under the mild curing conditions used. It was also presumed that the succinamic acid group was more reactive than ordinary primary amides. To confirm these hypotheses,

competitive cross-condensation reactions were studied between several amide model compounds and resole. These results are listed in Table I. When dodecanamide, octadecanamide, or succinamide was involved in the cross-condensation reaction, the weight percentage of the insoluble fractions recovered by solvent extraction were almost equivalent to those of the resole initially charged, although the nitrogen content in the insoluble fractions was a little higher than that in the products of resole self-condensation. The infrared spectra of the condensation mixtures revealed that the amide compounds had hardly reacted with resole.

On the other hand, succinamic acid or phthalamic acid showed a completely different cross-condensation behavior. By increasing the charges of these amides in cross-condensation, the insoluble fractions by solvent extraction decreased remarkably, suggesting that self-condensation of resole itself was suppressed by the presence of these amide compounds. That the nitrogen content in the insoluble fraction was much higher than that in the self-condensation products of resole also indicated that cross-condensation occurred predominantly between these amide compounds and resole. Prominent and specific infrared absorption bands of these amide compounds (3350 , 3150 , and 1640 cm^{-1}) disappeared and new imide absorption bands (1780 and 1695 cm^{-1}) appeared.

Compatibility between amide and resole could also be one of the important driving forces in cross-condensation. Dodecanamide was compatible with resole at 150°C , suggesting that the compatibility was not necessarily an essential condition for cross-condensation.

TABLE I
Competitive Cross-condensation Between Amide Compounds and Resole

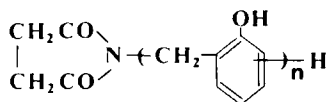
Amide	Charged composition (wt%)		Amide/resole (mol/g, $\times 10^{-3}$)	Insoluble fraction (wt%)	Nitrogen content ^a (wt%)
	Amide	Resole			
Dodecanamide	32	68	2.4	76	1.7
$\text{C}_{11}\text{H}_{23}\text{CONH}_2$	48	52	4.6	63	2.0
	58	42	6.9	47	2.0
Succinamide	21	79	2.3	79	2.5
CH_2CONH_2	35	65	4.6	63	2.0
CH_2CONH_2	50	50	8.6	48	2.0
Succinamic acid	21	79	2.3	65	3.2
CH_2CONH_2	35	65	4.6	9	3.6
CH_2CONH_2	45	55	7.0	1	—
CH_2COOH					
Phthalamic acid	28	72	2.4	47	2.9
$\text{C}_6\text{H}_4(\text{CONH}_2)(\text{COOH})$	42	58	4.4	0	—
$\text{C}_6\text{H}_4(\text{CONH}_2)(\text{COOH})$	53	47	6.8	0	—

^a In insoluble fractions. The nitrogen content in a cured resole was 1.5–1.8 wt%.

Separation and Identification of Cross-Condensed Oligomers

In the cross-condensation mentioned above between amide compounds and resole, condensation products were too numerous and complicated to be separated and identified. Therefore, 2-methylolphenol, the simplest derivative of resole, and succinamic acid were cross-condensed under the condition shown in Table II. A typical gel-permeation chromatogram of a cross-condensation mixture (run 2) is shown in Fig. 1. Peak 5 was confirmed as succinimide by comparing its elution time on a gel-permeation chromatogram, its ^{13}C -NMR spectrum, and its infrared spectrum with a well-identified reagent.

Field diffusion mass spectra of peaks 1–4 in Fig. 1 are shown in Fig. 2. The main signals were assumed to correspond to the following compounds:



- $n = 1$ (molecular weight, 205) : peak 4
 $n = 2$ (molecular weight, 311) : peak 3
 $n = 3$ (molecular weight, 417) : peak 2
 $n = 4$ (molecular weight, 523) : peak 1
 $n = 5$ (molecular weight, 629) : peak 1

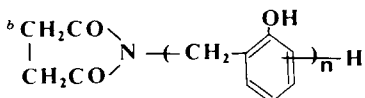
in which the phenol resin portion does not necessarily mean a linear structure.

The ^{13}C -NMR spectrum of peak 4 and the assignment of its signals are shown in Fig. 3. Significant infrared absorption bands of peak 4 were 3260 , 1775 , and 1690 cm^{-1} (imide) and 760 cm^{-1} (aromatic substitution). It was concluded from these results that the oligomer of peak 4 had a structure

TABLE II
Cross-condensation Between Amide Compounds and 2-Methylolphenol

Run	Charged composition ^a			Oligomers (g) ^b				
	SA (g)	MP (g)	SA/MP (mol/mol)	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n \geq 4$
1	2.34	4.32	0.02/0.04	0.16 (8.2)	1.34 (32.7)	1.03 (16.6)	1.01 (12.1)	2.06
2	3.51	3.24	0.03/0.03	0.51 (17.1)	1.65 (26.8)	1.35 (14.5)	0.97 (7.7)	1.14
3	4.68	2.16	0.04/0.02	0.86 (21.7)	1.46 (17.8)	0.70 (5.6)	0.57 (3.4)	1.06

^a SA: succinamic acid; MP: 2-methylolphenol.



Figures in brackets are yields in mol% on succinamic acid.

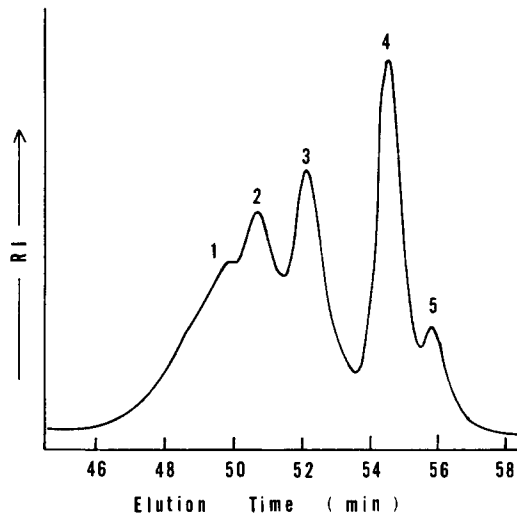


Fig. 1. Gel-permeation chromatogram of a cross-condensation mixture obtained from 30 mmol of succinamic acid and 30 mmol of 2-methylolphenol.

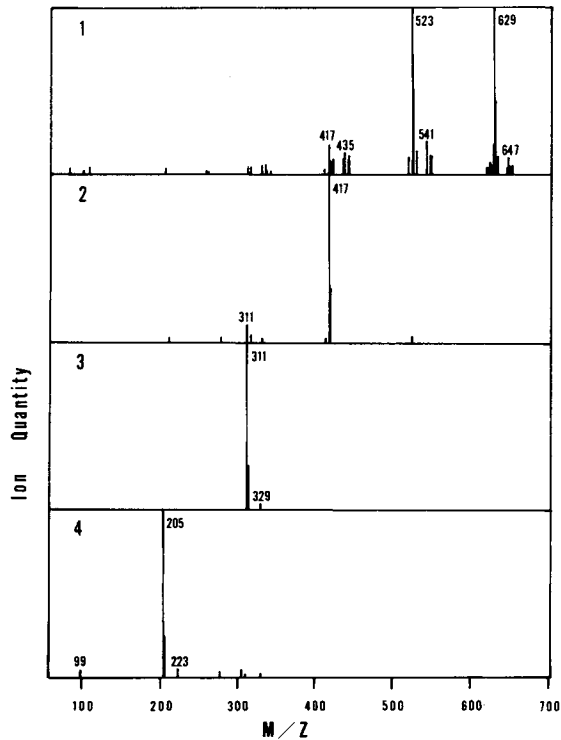


Fig. 2. Field diffusion mass spectra of peaks 1 through 4 separated from a cross-condensation mixture.

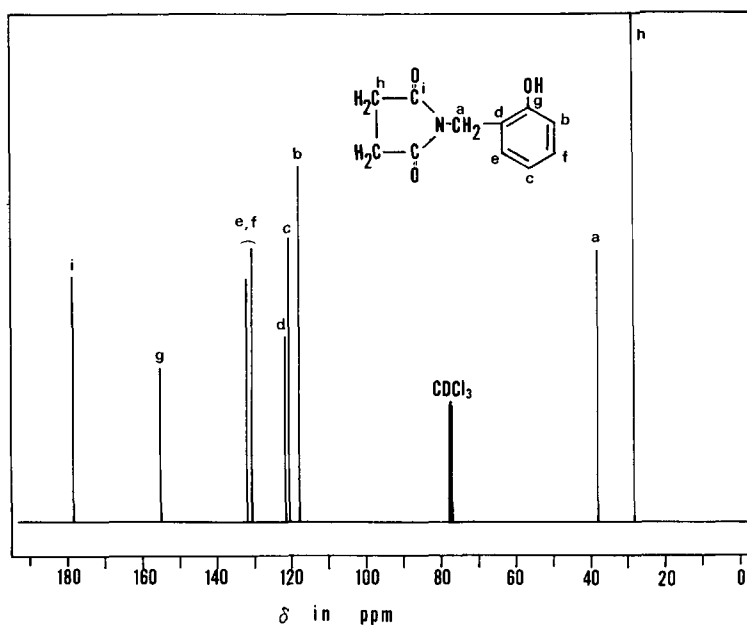
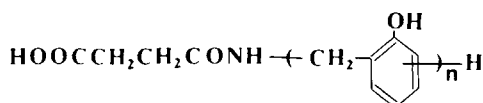
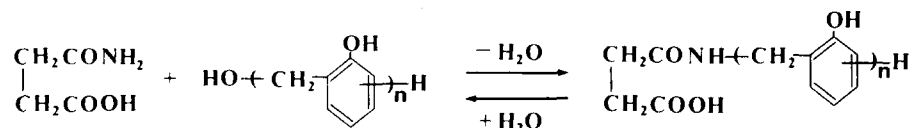
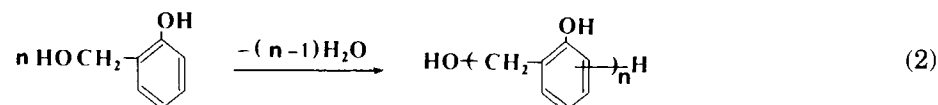
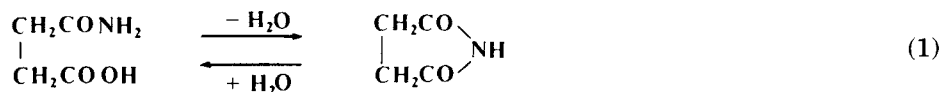


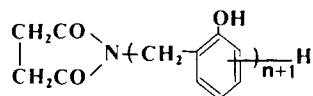
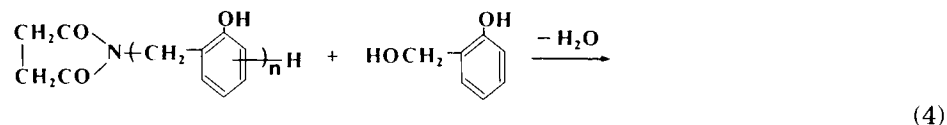
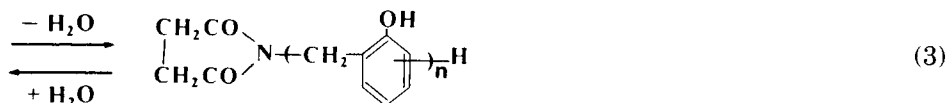
Fig. 3. ^{13}C -NMR spectrum of peak 4 separated from a cross-condensation mixture.

shown above ($n = 1$). Oligomers of peaks 1–3 were also presumed to have equivalent structures shown above ($n = 2, 3, 4, \dots$). Mass numbers 223, 329, 541, and 647 observed as small peaks in Fig. 2 were assumed to be the following ring-opened oligomers:



Yields and compositions of the oligomers determined by gel-permeation chromatography are listed in Table II. These results suggested a cross-condensation scheme involving the following reactions:





where $n = 1, 2, 3, \dots$

It is reported^{2,3} that imide compounds react with formaldehyde under acidic and basic conditions to form corresponding methylene or methylol derivatives, respectively. However, under the above condensation conditions, both phthalimide and succinimide showed no condensation tendency with 2-methylolphenol. That single nuclear oligomer was the prominent product in the reaction mixtures in Table II indicated that cross-condensation between succinamic acid and 2-methylolphenol was the predominant reaction in eqs. (1) through (4). In this case, condensation reactions were all carried out in an open system, so the equilibrium was favored toward the right.

CONCLUSION

By investigating model reactions, it was demonstrated that phthalamic acid and succinamic acid, in both of which amide and carboxylic acid groups are in the position to form an imide linkage, proved to be extremely reactive for condensation reaction with resole. The main reaction products were cross-condensed oligomers having an imide linkage. These observations suggested that the same mechanism was involved in the main cross-linking reaction of amidated polybutadienes with resole.

References

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