Preparation and Properties of Rubberlike High Polymers. II. Polymerization of Mixtures in Bulk*

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Synopsis — *Mixtures of butadiene and dimethylbutadiene with varying quantities of styrene and acrylonitrile have been copolymerized under various catalytic conditions at 100°C. The formation of cyclic dimers from dienes and vinyl compounds is, in some cases, much more pronounced than the dimerization of the dienes alone. Since the latter is also a kind of Diels-Alder reaction, a series with increasing dienophilic properties can be established from a comparison of the yields of cyclic dimers. From solubility and swelling experiments it is evident that the polymers prepared from butadiene and the vinyl compounds and those from dimethylbutadiene and acrylonitrile are true copolymers. The mechanical properties of the copolymers from butadiene and increasing amounts of a vinyl compound change gradually from those of a rubber to those of the polyvinyl compound. The copolymers from a mixture containing 30% styrene or acrylonitrile are very similar, respectively, to Buna S and Perbunan. Copolymers of the same composition from dimethylbutadiene and acrylonitrile, on the other hand, form a new class of thermoplastics with a much higher temperature of elasticity.*

INTRODUCTION

THE POLYMERIZATION of a homogeneous mixture, although more complicated than that of a single compound, involves easily reproducible reaction times, which is a considerable advantage when compared with the behavior of the same mixtures in emulsion. It is, therefore, frequently possible to produce a series of polymers of gradually changing composition from dienes and vinyl compounds which is suitable for study of the accompanying alterations in chemical and physical properties. Since such changes are not only affected by the initial ratio of diene to vinyl compound, but also by the experimental conditions (*e.g.*, temperature, catalyst, and yield), it is essential to evaluate kinetic conditions as a basis for comparison of the resulting polymers.

Three types of macromolecular compounds may be expected: (*1*) a true copolymer, (*2*) a purely mechanical mixture of separate polymers from the two components, and (*3*) a copolymer with a less regular pattern. As the rate of vinyl polymerization is higher than that of diene polymerization, catalytic conditions which favor the latter will increase the chances of copolymerization. The first aim of our kinetic study was, therefore, to find a regular change in reaction rates with increasing vinyl content. Since all polymers proved to be either soluble or strongly swelling in suitable solvents, true copolymers could be easily distinguished from mechanical mixtures by their interaction with these liquids. The results of these two sets of experiments (kinetic measurements and solubility determination) will be given in the sections on polymerization and on interaction with

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liquids. The comparison of these copolymers with the products obtained by polymerization in emulsion will be made in Part V of this series.

The polymerization of dienes is hampered by the formation of cyclic dimers, and the same type of reaction between dienes and vinyl compounds is more pronounced in most cases; some new results with the Diels-Alder reaction will also be described.

POLYMERIZATION OF MIXTURES

In Part I[1] of this series we discussed the reaction rates of 2,3-dimethylbutadiene, isoprene, butadiene, styrene, and acrylonitrile, polymerized (*1*) under the influence of natural impurities (heat polymerization), (*2*) with benzoyl peroxide (BP) as catalyst, and (*3*) with diazoaminobenzene (DAB) as catalyst. An investigation of all possible combinations would lead to at least 18 systems. The experiments which will be described refer only to combinations with butadiene, the base for Buna rubbers, and dimethylbutadiene, which is particularly easy to handle and purify. Some runs were first made with a mixture typical for certain Buna rubbers (diene:vinyl compound = 7:3) in order to study the influence of catalytic conditions; further experiments with increasing concentrations of the vinyl compound were made only under optimum conditions.

Butadiene–Styrene. Figure 1 gives a comparison of the rates for the mixture (7:3) and for the individual components. The reactivity of the mixture is comparable to that of pure butadiene. Yields, even in the presence of 1% DAB, are considerably less than 100%. From further preparatory experiments it is evident that the formation of cyclic dimers interferes with polymerization. Some of the butadiene, as well as some of the styrene, is used up by the dimerization reaction.

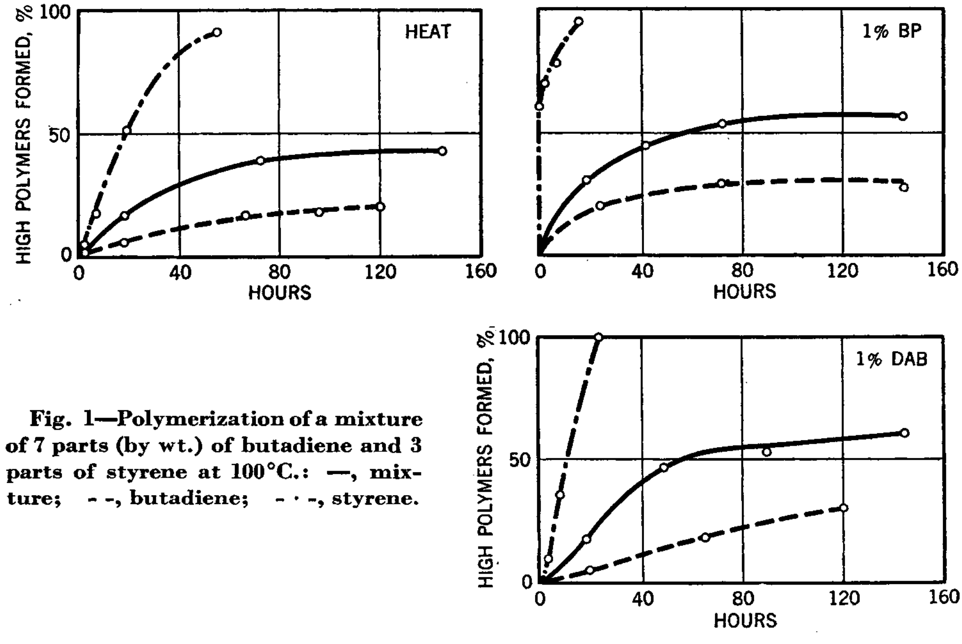

Fig. 1—Polymerization of a mixture of 7 parts (by wt.) of butadiene and 3 parts of styrene at 100°C.: —, mixture; - -, butadiene; - · -, styrene.

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[1] C. Koningsberger and G. Salomon, *J. Polymer Sci.*, 1, 200 (1946).

The resulting polymers differ from Buna S only by having a much larger soluble fraction, but this property is also a function of the reaction time.[1] The mechanical properties of the vulcanized samples are in reasonable agreement with those of Buna S.

Since the shape of the curves in Figure 2 indicates a very regular reaction course, the change of rate with increasing styrene concentration is expected to be gradual. The increase of yield with higher styrene concentration is caused by two factors: a higher reaction rate and a decrease in the dimerization reactions.

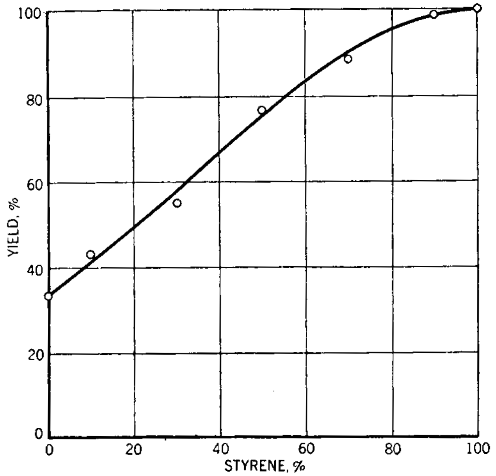

Fig. 2—Polymer yields from mixtures of butadiene with increasing quantities of styrene after 150 hours at 100°C., with 1% DAB as catalyst.

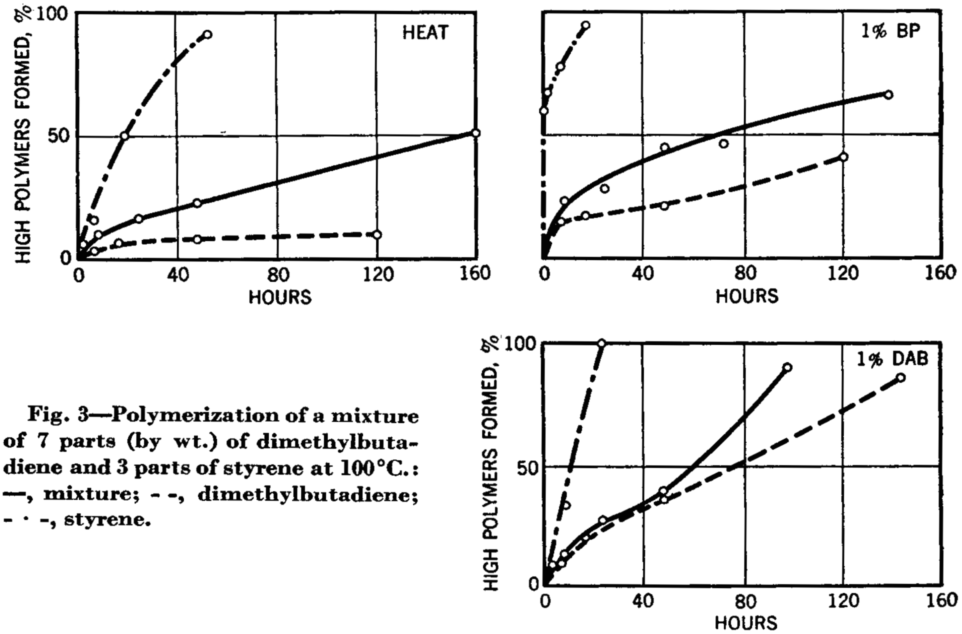

Fig. 3—Polymerization of a mixture of 7 parts (by wt.) of dimethylbutadiene and 3 parts of styrene at 100°C.: —, mixture; - -, dimethylbutadiene; - · -, styrene.

Dimethylbutadiene–Styrene. Figure 3 shows that styrene accelerates the heat polymerization of dimethylbutadiene; as a consequence, the formation of dimers is somewhat superseded by the polymerization reaction. The rate with 1% DAB is sufficiently high to yield 100% polymer within a reasonable time, as in the case of the pure diene.

The resulting polymers are all soft, soluble, and readily oxidized. Preliminary experiments with ethyl acetate as the solvent indicate that part of the yield consists of a mechanical mixture of polystyrene and methyl rubber. Further research was, therefore, temporarily discontinued.

Butadiene–Acrylonitrile. Corresponding experiments with acrylonitrile lead to somewhat unexpected results. As may be seen from Figure 4, the yields of heat polymers are very low, due to a rapid Diels-Alder reaction between butadiene and acrylonitrile, which supersedes, not only the polymerization, but also the formation of cyclic dimers from pairs of butadiene molecules. The addition of catalysts has sufficient effect on polymerization to produce Perbunan as the main yield.

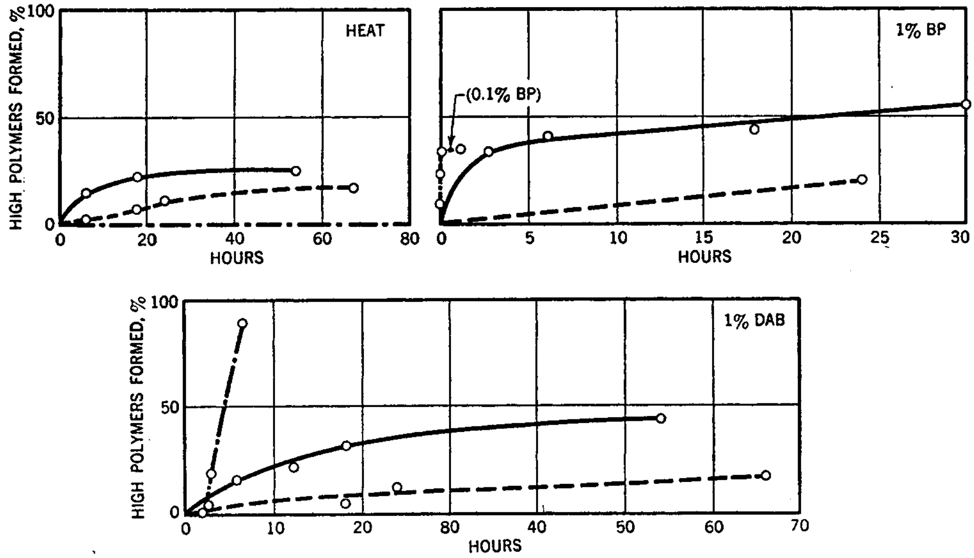

Fig. 4—Polymerization of a mixture of 7 parts (by wt.) of butadiene and 3 parts of acrylonitrile at 100°C.: —, mixture; - -, butadiene; - · -, acrylonitrile.

This Perbunan differs from the commercial product only by having a greater solubility in certain organic liquids. The vulcanized samples have properties very similar to those prepared from the commercial product.

We have seen (Fig. 4) that the addition of acrylonitrile has a highly accelerating effect on the polymerization of butadiene in the presence of catalysts. Nevertheless, in the range from 30% to about 80% nitrile content, the mixtures catalyzed by 1% DAB react more slowly than is accounted for by the nitrile content. This discrepancy is the cause of the peculiar S-shaped curve of Figure 5, as compared with the almost straight one of Figure 2. An explanation may, at least partly, be offered by the rapid Diels-Alder reaction between the diene and the nitrile, which competes strongly with the normal polymerization reaction. The nitrogen content of the polymers also indicates a loss of nitrile during the reaction (see Fig. 6).

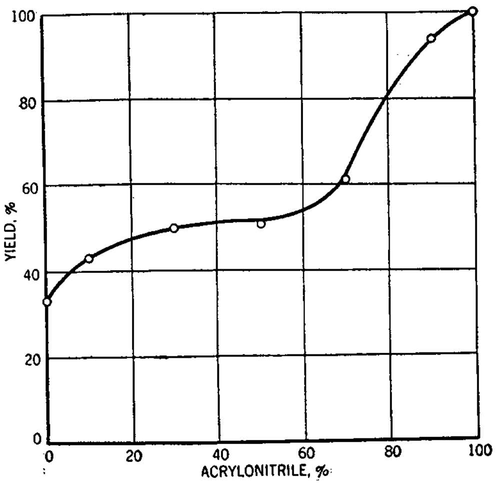

Fig. 5—Polymer yields from mixtures of butadiene with increasing quantities of acrylonitrile after 150 hours at 100°C., with 1% DAB as catalyst.

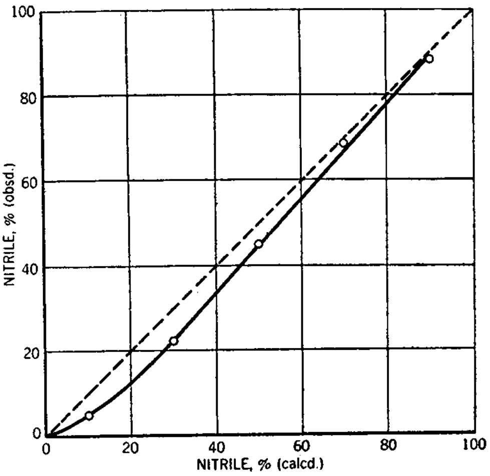

Fig. 6—Difference between observed and calculated nitrile contents for copolymers from Figure 5.

The properties of these polymers change gradually from those of a rubberlike substance at room temperature to those of a thermoplastic material which becomes elastic only at much higher temperatures. In the case of pure polyacrylonitrile this temperature is higher than the limit of thermal stability.

Dimethylbutadiene–Acrylonitrile. Analogous experiments with dimethylbutadiene

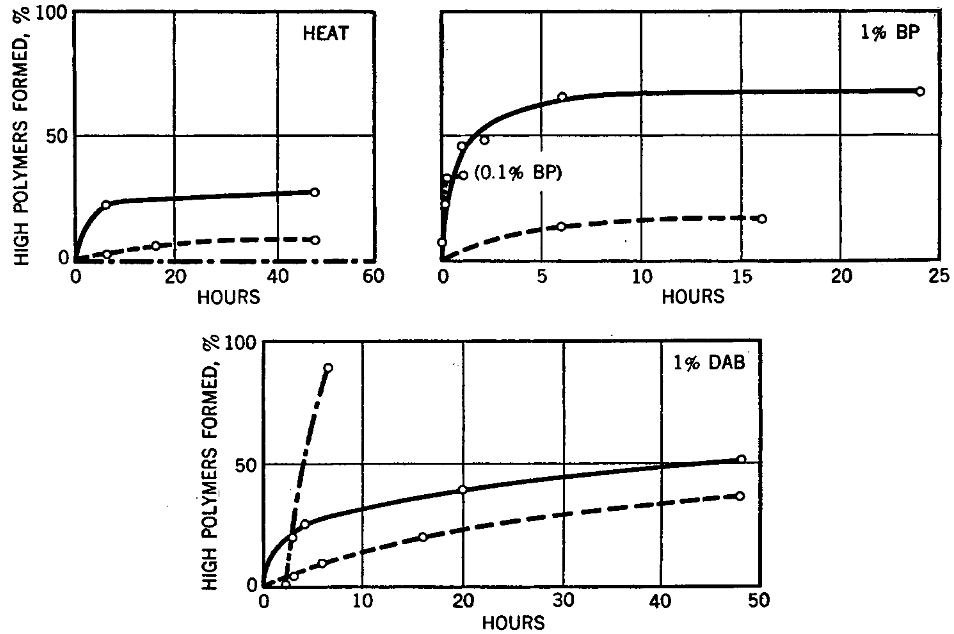

Fig. 7—Polymerization of a mixture of 7 parts (by wt.) of dimethylbutadiene and 3 parts of acrylonitrile at 100°C.: —, mixture; - -, dimethylbutadiene; - · -, acrylonitrile.

lead to kinetically comparable results. The polymerization is strongly catalyzed by BP and by DAB, but is interfered with by dimerization. This is not the case with dimethylbutadiene alone, catalyzed by DAB, and our experiments show that the rate of dimerization between the diene and the nitrile is again higher than that between two molecules of the diene (see Fig. 7).

The copolymers are soluble in strong solvents, *e.g.*, chloroform or toluene. Since polyacrylonitrile is insoluble and nonswelling in organic solvents, the possibility of formation of mechanical mixtures of methyl rubber and polymeric nitrile is excluded from these experiments. On the other hand, the polymers are completely precipitated by the addition of hexane to the solutions, which excludes the possibility of the presence of methyl rubber since the latter is soluble in this liquid.

The mechanical properties of these homologs of Perbunan are fundamentally different from those of Perbunan itself. At room temperature the polymers are hard and pliable, like gutta-percha, gradually showing increased elasticity at higher temperatures. These properties prove to be independent of the reaction time and of the method of preparation; more extensive experiments have, therefore, been made by polymerization in emulsion (Part III of this series).

DIELS-ALDER REACTION

The Diels-Alder reaction is an ordinary bimolecular one, the rate of which depends on the reactivity of both components, the dienes and the olefins. Since the three dienes used in these and the preceding experiments react both as olefins in the 1,2 or 3,4 position and as dienes, we can compare their reactivity with that of the vinyl compounds. Although typical differences may be observed, these reactions have a half-time of days or weeks at 100°C., which is very long compared to the time required for similar reactions with maleic acid anhydride, which have a half-time of seconds or minutes at 20°C. Such major differences are doubtless due to much smaller heats of activation for the latter reactions.

The results of the work described here and in Part I of this series[1] are compiled in Table I; the structure of the dimers is given in Figure 8.

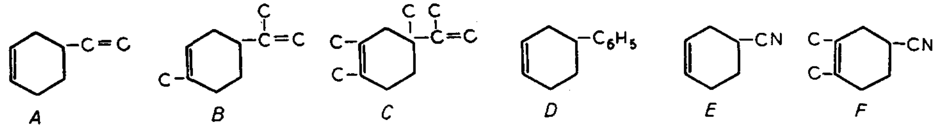

Fig. 8—Structures of possible dimers: *A*, dimeric butadiene; *B*, dimeric isoprene; *C*, dimeric dimethylbutadiene; *D*, Diels-Alder product from one butadiene and one styrene molecule; *E*, Diels-Alder product from one butadiene and one acrylonitrile molecule; and *F*, Diels-Alder product from one dimethylbutadiene and one acrylonitrile molecule.

Taking the accuracy of our data into account, we can establish three separate series of increasing dienophilic reactivity.

(*1*) From Table V of Part I[1] we note that 35% dimers are formed during the heat polymerization of butadiene. About the same yield is obtained (30%) when butadiene and styrene are copolymerized (in the ratio of 7:3) without a catalyst. Since, in this case, the dimeric fraction contains both possible compounds in the ratio of 6:4, we may say that the dienophilic reactivities of butadiene and styrene are of the same magnitude. On the other hand, when butadiene and acrylonitrile (7:3) are copolymerized without a

TABLE I

FORMATION OF DIMERS (DIELS-ALDER REACTION) AT 100°C. AFTER 100 HOURS

Components			Catalyst	Yield		Structure of dimers (Fig. 8) and composition of dimeric fraction
Diene	Vinyl compound	Ratio		Dimers, %	Polymers, %	
Butadiene	....	...	None	35	20	Exclusively *A*
			1% BP	30	30	
			1% DAB	25	40	
Isoprene	....	...	None	20	20	
			1% BP	..	40	Exclusively *B*
			1% DAB	..	40	
Dimethylbutadiene	....	...	None	10	20	
			1% BP	5	55	Exclusively *C*
			1% DAB	Traces	65	
Butadiene	Styrene	7:3	None	30	40	Mixture of about 60% of *A* and 40% of *D*
			1% BP	20	55	
			1% DAB	20	55	
Butadiene	Acrylonitrile	7:3	None	50	25	
			1% BP	25	60	Exclusively *E*
			1% DAB	40	40	
Dimethylbutadiene	Acrylonitrile	7:3	None	60	25	
			1% BP	25	60	Exclusively *F*
			1% DAB	30	50	

catalyst, a yield of 50% dimers is obtained; it appears, moreover, that the dimeric fraction consists almost exclusively of tetrahydrobenzonitrile. This means that the dienophilic reactivity of acrylonitrile is far greater than that of butadiene (about 10:1). We may accordingly give the following estimated rate relations with respect to the formation of cyclic dimers:

butadiene:styrene:acrylonitrile = 1:1:10

(*2*) The formation of cyclic dimers from dimethylbutadiene and acrylonitrile under the prevailing conditions of Table I is even more pronounced in the absence of catalysts than in the case of the lower homolog. We may, therefore, deduce the following ratio of dienophilic properties:

dimethylbutadiene:acrylonitrile = 1:10–15

(*3*) For the dimerization of the dienes themselves, the following ratios are derived from the values of Table I:

dimethylbutadiene:isoprene:butadiene = 1:2:3.5

Although no experiments were made with mixtures of the two dienes, the following complete series on the basis of increasing dienophilic properties is very probable from the data summarized above:

dimethylbutadiene	:	isoprene	:	butadiene	:	styrene	:	acrylonitrile
1	:	2	:	3.5	:	3.5	:	15–30

The slowest combination, *i.e.*, between two molecules of dimethylbutadiene, reacts with a half-time of weeks at 100°C., while the most reactive combination, between dimethylbutadiene and acrylonitrile, has a half-time of a few days at the same temperature. Differences between the two ends of the established series are, therefore, within a factor of 20. More accurate data are available from inhibition of polymerization, *e.g.*, by the addition of copper and manganese.[2] An attempt to offer a theoretical interpretation would be premature, since purely geometric factors may influence the rate, as well as changes in electronic arrangements.

It is evident that these side reactions make commercial production of such copolymers in homogeneous systems prohibitive. Polymerization in emulsion can be carried out at a much lower temperature, thereby greatly reducing the formation of cyclic dimers. This is one of the essential advantages of the emulsion method; the other important advantage is better heat dissipation in aqueous systems.

INTERACTION WITH LIQUIDS

The following experiments may serve as examples of the change in solubility and degree of swelling with increasing numbers of phenyl and nitrile groups in the polymers.

Butadiene–Styrene Copolymers. Toluene is a strong solvent for both separate polymeric components, butanone a strong solvent for polystyrene and a nonsolvent for polybutadiene, hexane a weak solvent for polybutadiene and a nonsolvent for polystyrene.

Minimum solubility in toluene occurs when there is cross linking of the polymers. Although the reaction times are the same, polymers with 30–70% styrene are formed much faster and are, therefore, "older" at the moment of isolation than those from butadiene. Polybutadiene, isolated after 240 hours, is as insoluble as these copolymers.[1] With decreasing concentration of butadiene in the monomeric mixture, the statistical chances for side reactions (causing cross linking) diminish and the copolymers remain soluble, although they are much "older" than the insoluble ones containing about 50% butadiene.

Solubility is a function of both the molecular size and the number of polarizable phenyl groups in the molecule. In the case of hexane only the smaller molecules of polybutadiene are soluble; the larger ones, which are soluble in toluene, remain in the gel fraction. The addition of only a few phenyl groups is sufficient to make all polymers insoluble in hexane.

Butanone is an associated liquid; in cases in which the ketone group can interact with a large number of polar or polarizable groups it acts as a solvent. As may be seen from Figure 9, a high concentration of phenyl groups, about one phenyl to three methylene groups, is necessary to dissolve all of the gel.

An even more significant picture is obtained from the swelling of the insoluble fraction. The weight fractions (the weight of swelling agent divided by the sum of the weight of swelling agent and the weight of polymers) are compared in Figure 10.

The interaction between toluene and the polymers now becomes essentially the same over the whole range of copolymers, while the fractions which are totally insoluble in hexane are still considerably swollen. The swelling in butanone is less significant, probably because the influence of molecular size and cross linking somewhat counterbalances that of the polar groups. On the whole, a comparison of vulcanized samples (which will be given in a later communication) is more conclusive because the effect of molecular size is cancelled out by uniform cross linking.

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[2] W. D. Wolfe (to Wingfoot Corp.), U. S. Pat. 2,217,632 (1940).

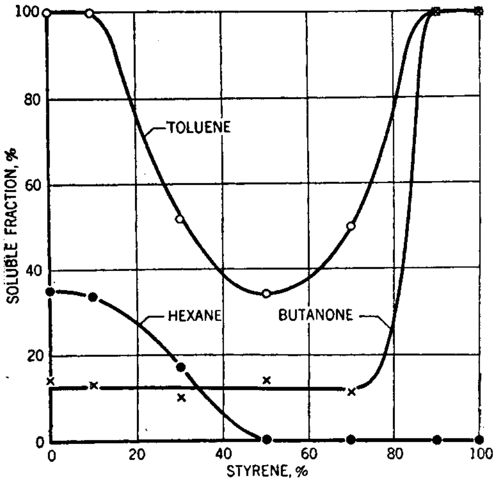

Fig. 9—Solubility at 20°C. for butadiene-styrene copolymers, prepared at 100°C. with 1% DAB, after 150 hours (see Fig. 2).

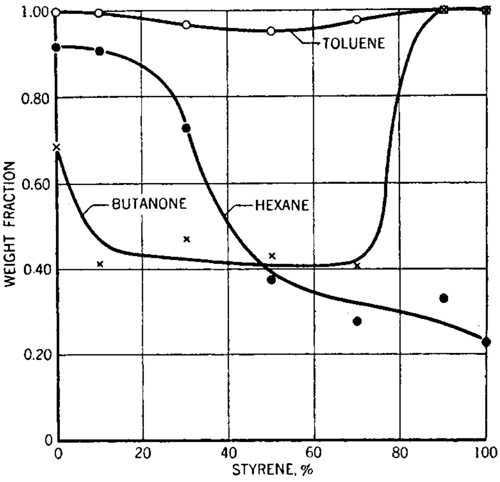

Fig. 10—Swelling of insoluble fraction (solvents are the same as in Fig. 9).

Butadiene-Acrylonitrile Copolymers. The situation is quite different for this system. The polymeric nitrile is not only insoluble, but also nonswelling, in all organic liquids at room temperature. In other words, a strong organic solvent for both components does not exist. The polymeric nitrile, however, is dissolved only by certain aqueous salt solutions (*e.g.*, lithium bromide, sodium thiocyanate, and zinc chloride),[3] which fact proves the two-dimensional structure of the macromolecules; those liquids, however, do not interact with the polymeric hydrocarbon. The most suitable solvent for the copolymers is chloroform which dissolves, for the greater part, polymers containing up to 50–60% nitrile. Unfortunately, no quantitative experiments have yet been performed and we are, therefore, adding a schematic curve to complete the picture (see Fig. 11).

We learn from Figure 11 that the presence of a few nitrile groups is sufficient to suppress solubility in these liquids. There are still great differences in the solvent action, as may be noted from the swelling equilibria given in Figure 12.

The interaction of the nitrile groups with the solvent decreases in the order: chloroform > butanone > toluene > hexane. The copolymers, which swell to an appreciable extent in the first three liquids, swell very slightly in hexane, a phenomenon typical for the oil-resistant properties of such rubberlike polymers.

These experiments show that differentiation between the effects of cross linking and the specific action of polar groups cannot always be made from solubility measurements alone, as may be seen from the properties of copolymers containing acrylonitrile. This case is, however, the only exception in the series of rubberlike copolymers and is due to the powerful associating forces of the nitrile groups. Because these groups are partly screened by the methyl groups in polymethyl acrylonitrile, the properties of this polymer must be comparable to those of polystyrene. It may be expected, therefore, that the whole range of copolymers containing methyl acrylonitrile will remain soluble or strongly swelling in chloroform and other weakly associated solvents. Detailed experiments with vulcanized samples will be described in further communications.

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[3] I. G. Farbenindustrie A.-G., German Pat. 631,527 (1936).

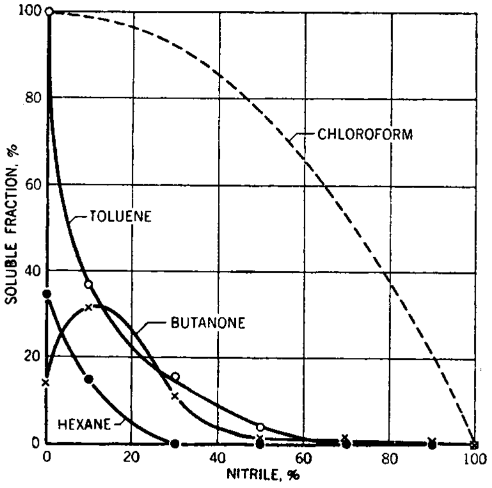

Fig. 11—Solubility at 20°C. for butadiene–acrylonitrile copolymers, prepared at 100°C. with 1% DAB, after 150 hours (see Fig. 5).

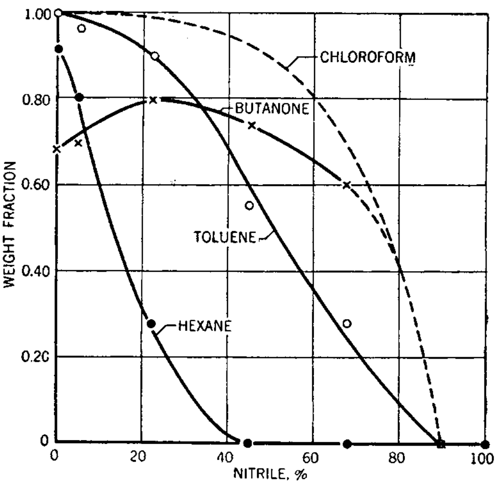

Fig. 12—Swelling of insoluble fractions. The solvents are the same as in Figure 11.

EXPERIMENTAL

The method of purification of the monomers and the polymerization procedure were the same as those described previously.[4] In some cases the polymers were precipitated with alcohol, while in others steam distillation proved to be more suitable for quantitative separation of the dimers.

The following examples may serve as an illustration.

Butadiene–Styrene. After heating for 150 hours at 100°C., the gaseous monomer was allowed to escape. The polymers were subjected to steam distillation and the resulting volatile compounds were fractionated after drying. The following fractions were separated:

Fraction	Temperature, °C.	Pressure, mm.	n_D^{20}
I	133–136	760	1.4918
II	136–147	760	1.5040
III	40–50	15	1.5233
IV	115	15	1.5420

The high-boiling fraction IV is identical with 1,2,5,6-tetrahydrodiphenyl (Formula *D*, Fig. 8), formed from one molecule of butadiene and one of styrene: carbon, 90.7% (calcd., 91.1%); hydrogen, 8.8% (calcd., 8.9%).

The lower boiling fractions contained monostyrene, some of which polymerized during redistillation. From fractions I–III a main fraction with the following properties was finally isolated: b.p.$_{760}$, 127.5–131.5°C.; n_D^{20}, 1.4720. Monostyrene[5]: b.p.$_{760}$,

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[4] C. Koningsberger and G. Salomon, *J. Polymer Sci.*, **1**, 200 (1946).

[5] H. I. Waterman and W. J. C. de Kok, *Rec. trav. chim.*, **53**, 1133 (1934).

145.4°C.; n_D^{20}, 1.5462; dimeric butadiene[6]: b.p.$_{760}$, 129.4°C.; n_D^{20}, 1.4637.

This fraction therefore contains the cyclic dimeric butadiene (Formula *A*, Fig. 8) which is formed simultaneously with the dimer from butadiene and styrene.

Butadiene–Acrylonitrile. The dimeric fraction consists entirely of one compound which proves to be 1,2,5,6-tetrahydrobenzonitrile. Elementary analysis: observed, C = 78.6%, H = 8.5%, N = 13.1%; calculated: C = 78.5%, H = 8.4%, N = 13.1%. B.p.$_{760}$, 192–196°C.; n_D^{20}, 1.4732 (according to literature[7]); b.p.$_{760}$, 188–192°C.; n_D^{20}: 1.472 (Formula *E*, Fig. 8). Contrary to the results of the first experiment, no dimeric butadiene is present.

Dimethylbutadiene–Acrylonitrile. The product was precipitated with alcohol, separated, and fractionated. Only one high-boiling compound was found: b.p.$_{760}$, 217–222°C.; n_D^{20}, 1.4795.

The nitrogen content is in agreement with the assumed structure of 1,2,5,6-tetrahydro-3,4-dimethyl benzonitrile: N = 10.1% (calcd., 10.4%), see Formula *F*, Figure 8.

Acknowledgment

The authors wish to thank J. W. F. van't Wout for his assistance in carrying out the laboratory experiments.

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[6] J. B. Harkness, G. B. Kistiakowski, and W. H. Mears, *J. Chem. Phys.*, **5**, 682 (1937).

[7] W. D. Wolfe (to Wingfoot Corp.), U. S. Pat. 2,217,632 (1940).