Soluble Copolymers of Diallyl Monomers

WALTER H. SCHULLER[1], J. A. PRICE[2], S. T. MOORE, and W. M. THOMAS
Stamford Laboratories, Research Division, American Cyanamid Co., Stamford, Conn.

Copolymers containing amino groups are useful in diverse fields such as ion exchange, flocculation, paper stock treatment, and synthetic fibers. While investigating methods for producing such polymers, the authors found that certain diallyl compounds gave soluble copolymers rather than the anticipated gels. This article discusses the relationship of monomer structure to polymer properties, confirming and extending the preceding publications by Butler and others (*2–7, 9, 10*). Some applications of soluble copolymers are described.

When diallyldimethylammonium chloride was copolymerized with acrylonitrile or with acrylamide, the copolymer contained substantial amounts of quaternary compound, yet dissolved in a suitable liquid with no trace of gel. Table I provides examples of this behavior, listing a series of acrylamide copolymers prepared by redox polymerization in water. Solution viscosities were high, indicating molecular weight of the order of one million. Analysis of the copolymer's showed that substantial amounts of quaternary compound had been incorporated but without appearance of pendant double bonds.

Some of these copolymers were tested as strengthening agents for paper. Paper fibers in aqueous suspensions develop a negative charge; hence, cationic materials, particularly polycationic polymers, tend to be irreversibly adsorbed at the fiber surface. Nonionic or anionic polymers are not adsorbed to the same extent unless mordants such as alum are used. Paper is made from very dilute slurries (0.1 to 0.6% on paper machines, 0.035% on laboratory equipment), so the adsorption mechanism must be efficient for economic utilization of chemical additives to the fiber slurry. These copolymers do improve the strength of paper substantially (Table II). Other results not listed show that the polymers are effective over a wide pH range.

Table II also shows that the products are true copolymers. Paper stock slurries were treated with a solution containing 10% polyacrylamide and 2% monomeric diallyldimethylammonium chloride. Physical properties of the handsheets were not improved, indicating that polymer must contain chemically bonded cationic groups to be effective.

Copolymers of the same allyl monomer with acrylonitrile are listed at the top of Table III. Nitrogen analyses showed that the copolymers contained about one half as much allyl compound as was present in the monomer charge. The presence of basic sites was confirmed by a dye adsorption test. Copolymers were of fairly high molecular weight (roughly 100,000 to 300,000 range), but were soluble in dimethylformamide and in aqueous sodium thiocyanate. The 87–13 copolymer was spun successfully into fibers. In this instance an approximately 10% polymer solution in 50% sodium thiocyanate was extruded through a spinnerette into water at about 0° C. The fiber was washed, stretched, and dried. It had typical properties for an acrylic fiber.

Experiments with other allyl compounds, also listed in Table III, show that the ability to form high molecular weight, soluble copolymers is a general property of diallyl compounds of this class. On the other hand, if three or four allyl groups were attached to nitrogen, the products gave gels in dimethylformamide and were presumably cross-linked. A sulfur compound also gave a soluble copolymer.

N,N-Diallylmelamine is a monomer that can lead to soluble or to insoluble copolymers depending on the reaction conditions. In water at low pH, the products tend to be gels, whereas soluble copolymers are formed under nonacidic conditions (Table IV).

EXPERIMENTAL

Materials. The allyl amines were obtained from Shell Development Co. Vinyl acetate was from Carbide and Carbon Chemicals Co. Acrylamide, acrylonitrile, *N,N*-diallylmelamine and Calcocid Alizarin Blue SAPG dye were from American Cyanamid Co. Diallylmethylamine was prepared by the reaction of allyl chloride with methylamine and was converted in turn to the oxide with hydrogen peroxide at room temperature. Quaternary salts were made by reaction of an allyl halide with a tertiary amine (which might possess one or more allyl groups) as described by Butler and others (*3,4*).

Diallyl sulfide (Eastman Kodak Co.) was converted to $(CH_2{=}CHCH_2)\overset{\oplus}{S}CH_3$, $\overset{\ominus}{CH_3SO_4}$ by reaction with dimethyl sulfate at room temperature in methanol by the procedure of Butler and Benjamin (*3*). The product was obtained as an oil by adding ether.

Polymerization. Preparation of acrylamide copolymers is illustrated by the procedure used for Polymer A of Tables I and II. A flask was charged with 55 ml. of water and 69.4 grams of

Table 1. Copolymers of Acrylamide with Diallyldimethyl Ammonium Chloride[a]

% Allyl Compound in Monomer Mixture	Catalyst, % of Total Monomers		% Conversion (from Iodine Number)	Brookfield Viscosity of 10% Solution[b] Cps. at 25° C.	Polymer Identification (see Table II)
	$(NH_4)_2S_2O_8$	$K_2S_2O_5$			
25	0.09	0.045	83	14,000	A[c]
15	0.15	0.085	81	40,000	
10	0.13	0.065	92	70,000	B[d]
6	0.12	0.06	. . .	> 100,000	
6	0.40	0.20	96	51,400	
3	0.07	0.035	. . .	> 100,000	
1	0.34	0.17	98	28,000	C

[a] Prepared at 40° C. in water as described.

[b] For polyacrylamide 15,000 cps. corresponds roughly to molecular weight 700,000 and 100,000 cps. to 1,500,000.

[c] Precipitated and purified sample analyzed as follows: N, 17.4%; Cl, 2.9%; microhydrogenation over platinum oxide showed no uptake; no C=C by infrared; 12.8% quaternary by titration; iodine absorption 0.4 cg. I/g. These measurements indicate a quaternary content of 12 to 13% and little residual unsaturation.

[d] Combination of iodine number and polarography indicated about 7.5% allyl compound in the copolymer.

Table II. Effect of Copolymers on Paper Properties

(Acrylamide–diallyldimethylammonium chloride copolymers)

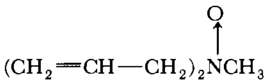
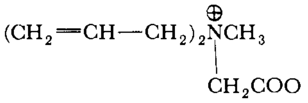
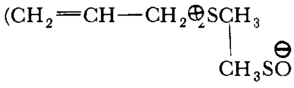
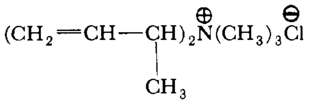
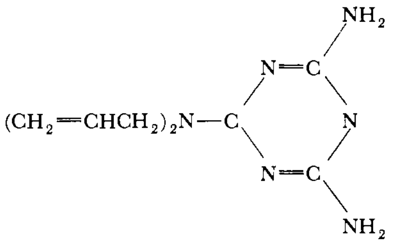
Polymer Added		Pulp Type	Alum, % of Pulp	pH of Pulp Suspension	Tensile, Lb./In.	Burst, P.S.I.
Identification (see Table I)	% of pulp					
None	. . .	Bleached northern kraft	0	4.5	30.3	. . .
A	3.0		0	4.5	31.9	. . .
B	3.0		0	4.5	34.9	. . .
None	. . .	Sulfite-soda	0	7.0	15.5	23.0
C	2.0		0	7.0	17.6	27.6
C	2.0		2	7.0	18.9	28.1
None	. . .		0	4.7	12.1	20.0
Polyacrylamide	10.0					
Diallyl monomer	2.0		0	7.0	12.8	20.4

---

[1] Present address, U. S. Department of Agriculture, Naval Stores Station, Olustee, Fla.

[2] Present address, American Viscose Co., Marcus Hook, Pa.

Table III. Copolymers with Acrylonitrile

Allyl Comonomer	% of Monomer Charge Acrylonitrile	 Vinyl acetate	 Allyl compd.	Catalyst, % of Monomers $NaClO_3$	 $Na_2SO_3 \cdot 7H_2O$	 HNO_3	% Yield	Solution Viscosity[a] If Soluble	Dye Test
$(CH_2{=}CH{-}CH_2)_2\overset{\oplus}{N}(CH_3)_2\overset{\ominus}{Cl}$	90	. . .	10	0.43	3.06	1.14	71	33.1	Positive
$(CH_2{=}CH{-}CH_2)_2\overset{\oplus}{N}(CH_3)_2\overset{\ominus}{Cl}$	87	. . .	13	0.65	2.33	4.62	52	16.3	Positive
$(CH_2{=}CH{-}CH_2)_2\overset{\oplus}{N}(CH_3)_2\overset{\ominus}{Cl}$	75	. . .	25	0.65	2.33	3.30	34	12.0	Not tested
$(CH_2{=}CHCH_2)_3NCH_3\overset{\ominus}{Br}$	85	5	10	0.88	3.15	2.27	65	Gel	Not tested
$(CH_2{=}CHCH_2)_4\overset{\oplus\ominus}{NBr}$	90	. . .	10	1.19	4.26	3.08	62	Gel	Not tested
$(CH_2{=}CHCH_2)_2NH$	85	5	10	0.85	3.06	8.62	71	27.7	Positive
$(CH_2{=}CHCH_2)_2NCH_3$	85	5	10	0.85	3.06	7.70	72	20.4	Not tested
 $(CH_2{=}CH{-}CH_2)_2\overset{O\uparrow}{N}CH_3$	85	5	10	0.85	3.06	6.22	64	22.7	Not tested
$(CH_2{=}CH{-}CH_2)_3N$	85	5	10	0.85	3.06	6.90	63	Gel	Not tested
 $(CH_2{=}CH{-}CH_2)_2\underset{CH_2COO}{\overset{\oplus}{N}}CH_3$	85	5	10	0.85	3.06	2.21	81	19.3	Not tested
 $(CH_2{=}CH{-}CH_2\overset{\oplus}{S}\underset{CH_3\overset{\ominus}{SO_4}}{C}H_3$	85	5	10	0.85	3.06	2.02	63	18.6	Positive
 $(CH_2{=}CH{-}\underset{CH_3}{C}H)_2\overset{\oplus}{N}(CH_3)_3\overset{\ominus}{Cl}$	85	5	10	0.88	3.15	2.27	32	. . .	. . .
$(CH_2{=}CH{-}CH_2)_2S^2$	90	. . .	10	. . .	. . .	. . .	. . .	Gel	Positive
	95	. . .	5	3.4 $(NH_2)_2S_2O_8$	0.7 $Na_2S_2O_5$	1.3 H_2SO_4	76	Gel	Positive

[a] Viscosity in centipoises at 40° C. of a solution containing 1 g. polymer in 100 ml. of aqueous solution containing 57.5% NaSCN in water.

[b] Polymerized in benzene at 80° C. with 1.0% azobisisobutyronitrile. All others polymerized as described.

a 36% aqueous solution of diallyldimethylammonium chloride. The mixture was adjusted to pH 2.5 with a few drops of 6*N* sulfuric acid. Three dropping funnels contained the following: (1) a solution of 75.0 grams of acrylamide in 200 ml. of water, (2) a solution of 0.090 grams of ammonium peroxydisulfate in 50 ml. of water, and (3) a solution of 0.045 grams of potassium pyrosulfite in 50 ml. of water. The flask and contents of the funnels were added in 8 equal portions over a 1-hour period. Reactants were maintained at 40° C., and vigorous stirring was continued under nitrogen. After 4 additional hours, the solution was diluted with 500 ml. of water and cooled.

In the experiments listed in Table IV, the components were all mixed at the start, and reacted at the indicated temperature.

Acrylonitrile copolymers were made in a similar way. Mixed monomers were placed in the flask along with enough water and dilute nitric acid to give a 10% solution of pH 2.3. A mixture of sodium chlorate and sodium sulfite heptahydrate in one dropping funnel and nitric acid in the other were added over a 2-hour period. Table III lists the amounts. After 2 hours' additional reaction at 40° C. under nitrogen, the slurry was filtered, washed, and dried.

Dye Test. One gram of dry copolymer was boiled for 30 minutes in 100 ml. of a solution containing 0.04 grams of sulfuric acid, 0.20 grams of sodium sulfate and 0.04 grams of Calcocid Alizarin Blue SAPG (Colour Index No. 1054). After thorough washing, homopolymer of acrylonitrile showed no coloration, whereas copolymers with basic groups were dyed blue.

Preparation of Handsheets. Paper pulp was slurried with demineralized water (3 kg. per 106 liters) in a 5-pound Valley beater and then beaten for 30 minutes with a 31-pound load on the bed plate lever arm. The freeness (Green) of the bleached northern kraft stock was 500 ml. and that of the 60-40 bleached sulfite-bleached soda was 350 ml. The stock was diluted to 0.6% consistency, and aliquots were treated with requisite amounts of dilute polymer, hydrochloric acid, sodium hydroxide, or alum solutions. Handsheets were made on a Nash sheet machine using demineralized water adjusted to the desired pH value for deckle dilution. All pH measurements were made with

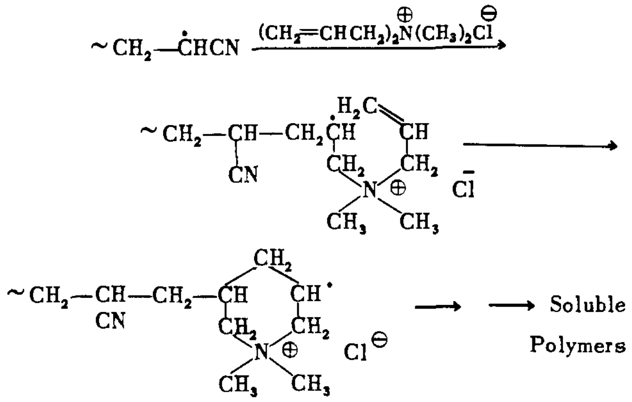
Table IV. N,N-Diallylmelamine–Acrylamide Copolymers

Diallylmelamine, % of Total Monomer	Solvent	Ratio, Solvent: Monomers	Other Components (as % of Monomers)	Reaction Conditions		Product
				°C.	Min.	
5	Water	10	1% $(NH_4)_2S_2O_8$ HCl to pH 2-2.5	65	10	Gel
10	Water	4	0.1% $(NH_4)_2S_2O_8$ HCl to pH 2.8	60-65	35	Near gel (at 65% conv.)
10	Dioxane	4	0.2% benzoyl peroxide	95-100	15	White solid, soluble in water
50	Dioxane	4	0.5% benzoyl peroxide	to 100°	120	White solid (29% diallyl-melamine), soluble in 1 to 1 acetone-water

a glass electrode pH meter. The sheets were pressed between blotters, dried for 1 minute at 122° C., and conditioned at 73° F. and 50% relative humidity. Basic weight, tensile strength and bursting strength measurements were made using TAPPI standard methods. Strength values were corrected to a 50-pound basis weight.

DISCUSSION

The unusual ability of certain diallyl compounds to give soluble copolymers is explained as recurring formation of six-membered rings (*2-7*). Copolymerization with acrylonitrile, for example, is depicted as follows:



In *N,N*-diallylmelamine, charge and bond angle at the allyl nitrogen atom may determine whether cyclic polymerization is preferred. The ultraviolet absorption spectra (Figure 1) are interpreted by R. C. Hirt and R. G. Schmitt of this laboratory as being consistent with the structures shown below.

Such forms are considered likely by analogy with those of melamine and some related oxygenated compounds (*1,8*). Only the structure shown above may be capable of polymerizing exclusively through the cyclic route.

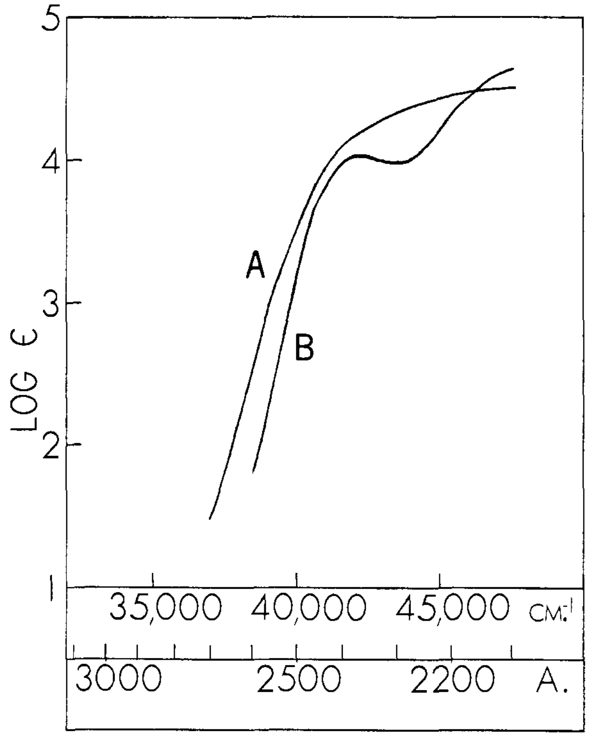
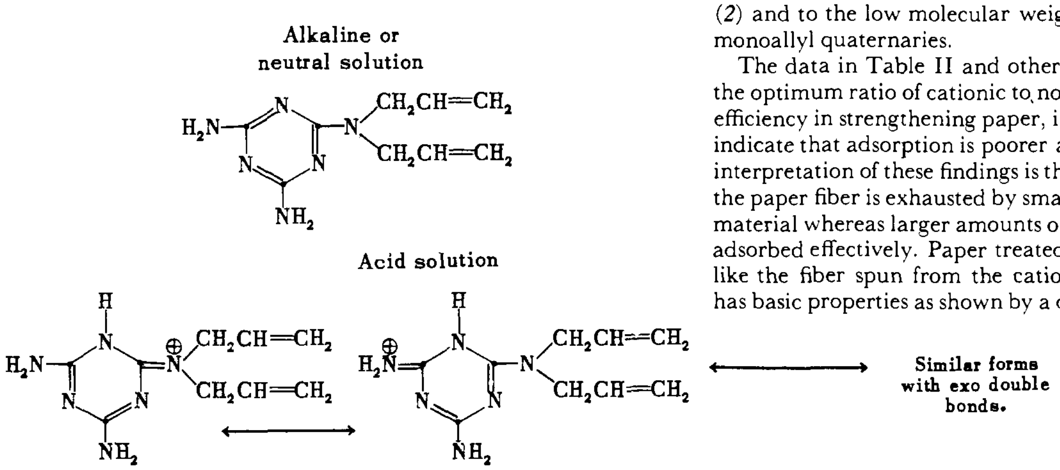


Figure 1. Ultraviolet absorption spectrum of N,N-diallylmelamine in water (*A*) and in 0.1*N* hydrochloric acid (*B*)

Butler and Angelo (*2*) obtained a gel from diallylamine hydrochloride homopolymerized at 60° C. in concentrated solution with *tert*-butyl hydroperoxide. In later work (*5*), a saturated, soluble homopolymer was obtained. The authors' soluble copolymer with acrylonitrile probably reflects the mild polymerizing conditions favoring the cyclic route.

Apparently, the amount of diallyl compound entering the copolymer is greater than with monoallyl amines, and the amount of degradative chain transfer is less. Molecular weights of these copolymers are in the hundred thousand to million range as contrasted to the few-thousand range for allyl homopolymers (*2*) and to the low molecular weights generally obtained with monoallyl quaternaries.

The data in Table II and other results not listed show that the optimum ratio of cationic to nonionic groups, for maximum efficiency in strengthening paper, is very low. Nitrogen analyses indicate that adsorption is poorer as the ratio is increased. One interpretation of these findings is that the adsorptive capacity of the paper fiber is exhausted by small amounts of highly cationic material whereas larger amounts of less cationic material can be adsorbed effectively. Paper treated with the cationic polymers, like the fiber spun from the cationic acrylonitrile copolymer, has basic properties as shown by a dye staining test (*11*).



ACKNOWLEDGMENT

The authors are indebted to Albert Blockman for measurement of the physical properties of handsheets, to C. A. Davis and Oscar Tukes for making the handsheets, and to R. P. Smith and J. A. Kuck and their staffs for analyses. Influence of reaction pH on polymer solubility was first noted by Jun Jen, who obtained the data of Table IV.

LITERATURE CITED

(1) American Cyanamid Co., New Products Bull. "N,N-Diallylmelamine," 1956.
(2) Butler, G. B., Angelo, R. J., *J. Am. Chem. Soc.* **79,** 3128 (1957).
(3) Butler, G. B., Benjamin, B. M., *Ibid.*, **74,** 1946 (1952).
(4) Butler, G. B., Bunch, R. L., *Ibid.*, **71,** 3122 (1949).
(5) Butler, G. B., Cranshaw, A., Miller, W. L., *Ibid.*, **80,** 3615 (1958).
(6) Butler, G. B., Goethe, R. L., *Ibid.*, **76,** 2419 (1954).
(7) *Chem. Eng. News* **35,** 22 (March 11, 1957).
(8) Hirt, R. C., Schmitt, R. G., *Spectrochim. Acta* **12,** 127 (1958).
(9) Marvel, C. S., Stille, J. K., *J. Am. Chem. Soc.* **80,** 1740 (1958).
(10) Simpson, W., Holt, T., Zeite, R., *J. Polymer Sci.* **10,** 489 (1953).
(11) Stafford, R. W., Thomas, W. M., Williams, E. F., Woodberry, N. T., *Paper Trade J.* **120,** 155 (1945) (TAPPI Section).

RECEIVED for review January 2, 1959. Accepted March 16, 1959.

Safe Processing Curing Systems for Viton Fluoroelastomers

A. L. MORAN, R. P. KANE, and J. F. SMITH
E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

Further details on specific curing agents will be found in the article of the same title on page 831, July 1959 I/EC.

The combination of vinylidene fluoride and hexafluoropropylene represented in Viton has been carefully chosen to give good processing compounds and high quality vulcanizates. However, the proper utilization of any elastomer is dependent, to a large extent, on the development of safe processing curing agents. The following tables contain data obtained with a number of materials as curing agents for Viton A and Viton A-HV. The influence of these curing agents on processing safety as well as original and aged vulcanizate properties is shown.

Unless otherwise specified in the tables, the press cure is 30 minutes at 300° F., and the oven cure is step cure to 400° F. and 24 hours at 400° F.

RECEIVED for review March 9, 1959. Accepted April 2, 1959.

Table I. Triethylenetetramine and Benzoyl Peroxide as Curing Agents for Viton A

Compound	A-1	B-1
Viton A	100	100
Zinc oxide	10	10
Dibasic lead phosphite [a]	10	10
MT carbon black	20	...
Fine silica-silicone oil (100/20) [b]	...	20
Triethylenetetramine	1	...
Benzoyl peroxide	...	2
Mooney scorch at 250° F. (MS)		
Minutes to a 10-point rise	2	3
Stress-strain, original		
Modulus at 100%, p.s.i.	1180	360
Modulus at 200%, p.s.i.	...	580
Tensile strength, p.s.i.	2650	2250
Elongation at break, %	180	720
Hardness, shore A	75	75

[a] Dyphos, National Lead Co., New York 6, N. Y.
[b] HiSil 233, Columbia Southern Chemical Corp., Pittsburgh, Pa. LM-3 oil, Silicone Products Division, Union Carbide Corp.

Table II. Hexamethylenediamine Carbamate as a Curing Agent for Viton An and Viton A-HV

Compound	A-2	B-2	C-2	D-2	E-2
Viton A	100	100	100	...	...
Viton A-HV	...	...	...	100	100
Zinc oxide	10	...	...	...	...
Dibasic lead phosphite	10	...	...	...	...
Magnesium oxide [a]	...	15	15	15	15
MT carbon black	20	20			
MT carbon black	20	20	60	20	60
Hexamethylenediamine carbamate [b]	1	1	1	1	1
Mooney scorch at 250° F. (MS)					
Minutes to a 10-point rise	36	12	9	7	6
Stress-strain, original					
Modulus at 100%, p.s.i.	370	310	950	390	1200
Modulus at 200%, p.s.i.	1040	860	1880	1130	...
Tensile strength, p.s.i.	2450	2325	2200	2500	2400
Elongation at break, %	340	340	200	320	170
Hardness, shore A	67	68	87	67	85

[a] Darlington 601, Darlington Chemical Co., Philadelphia, Pa.
[b] Diak No. 1, E. I. du Pont de Nemours & Co., Inc.

Table III. Ethylenediamine Carbamate as a Curing Agent for Viton A-HV

Compound	A-3	B-3	C-3	D-3
Viton A-HV	100	100	100	100
Magnesium oxide [a]	15	15	15	15
MT carbon black	20	20	20	60
Hexamethylenediamine carbamate	1	...	...	...
Ethylenediamine carbamate [b]	...	0.85	1.0	0.85
Mooney scorch at 250° F. (MS)				
Minutes to a 10-point rise	7	36	25	32
Stress-strain, original				
Modulus at 100%, p.s.i.	390	350	380	1050
Modulus at 200%, p.s.i.	1130	1190	1330	...
Tensile strength, p.s.i.	2500	2875	2875	2600
Elongation at break, %	320	350	320	190
Hardness, shore A	67	69	68	84
Compression set, Method B				
70 hours at 250° F.	35	34	23	32
Stress-strain, after 5 days at 500° F. (oven)				
Tensile strength, % retained	57	59	68	62
Elongation, % retained	97	92	81	105
Hardness, change	+6	+7	+8	+5

[a] Darlington 601.
[b] Diak No. 2, E. I. du Pont de Nemours & Co., Inc.