

## Photosensitive Azide Polymers\*

STEWART H. MERRILL and C. C. UNRUH, *Research Laboratories, Eastman Kodak Company, Rochester, New York*

### INTRODUCTION

Organic azides are known to decompose photolytically, as well as thermally, with the evolution of nitrogen.<sup>1,2</sup> The imine "radical"  $(R-)\bar{N}$  which remains couples rapidly with another imine or with some other molecule of the environment. With the azide group on a polymer, the decomposition and coupling could result in crosslinking, if there is no solvent or other material present with which the coupling can preferentially occur. If the polymer crosslinks on exposure to light, a photographic image is available. By exposure of a thin layer through a negative the polymer will be selectively crosslinked and insolubilized in the image areas. The unexposed polymer can be removed with a solvent. The preparation and examination of polymers made photoreactive by the attached aromatic azide groups was the object of the work reported here.

To form the azide group on an aromatic ring requires a series of reactions. Difficulties in handling and characterization of the product are encountered if the series of reactions are carried out on the polymer, unless it is of very low molecular weight. The units of the polymer which undergo side reactions or do not react are carried along and cannot be separated from the desired product. For this reason it was difficult to obtain a well-defined product from the preparation of polyazidostyrene starting with polystyrene.

A better route to azide polymers is to form the azide on a simple molecule which is then united with the polymer by means of a reactive function. Copolymers of maleic anhydride were useful since they react with amines and alcohols. Also, poly(vinyl alcohol) and cellulose derivatives with free hydroxyl groups react with acid chlorides and anhydrides. These are the polymers which are described in this paper.

Only aryl azides were used. They are easy to prepare and are thermally more stable than alkyl azides. The bad reputation of azides derives mostly from metal salts and alkyl compounds. Most aromatic azides decompose without violence between 100 and 175°C.

\* Communication No. 2239 from the Kodak Research Laboratories.

## EXPERIMENTAL

### Azide Compounds\*

All of the aromatic azides were made by diazotization of the corresponding amine, followed by treatment with sodium azide. The preparation of 3- and 4-azidophthalic acid has been described, and this general method was employed in each case.<sup>3</sup>

*3-Azidophthalic anhydride.* The azidophthalic acid<sup>3</sup> was cyclized by heating at gentle reflux in a mixture of equal parts of acetic anhydride and benzene. Following evaporation *in vacuo* to near dryness, the residue was recrystallized from carbon tetrachloride. It melted, with decomposition, at 124–126°.

ANAL. Calcd. for  $C_8H_5O_2N_3$ : N, 22.2%. Found: N, 22.5%.

*4-Azidophthalic anhydride.* This isomer was made from the acid in the manner just described. After crystallization from carbon tetrachloride, it melted at 88–89°.

ANAL. Found: N, 22.4%.

*3-, 4-Azidophthalic anhydride, mixed isomers.* A mixture of approximately equal parts<sup>†</sup> of the two isomers was the final product of a synthetic sequence starting with the nitration of phthalic acid. The isomer mixture was carried along without separation. The product was isolated as described for 3-azidophthalic anhydride.

*p-Azidobenzoyl chloride.* *p*-Azidobenzoic acid,<sup>4</sup> m.p. 180–182° (dec.) after recrystallization from aqueous methanol, was heated with an excess of thionyl chloride. Recrystallization from ligroin at ice temperature yielded the acid chloride, m.p. 57–58°.

*m-Azidobenzyl alcohol.* *m*-Nitrobenzyl alcohol was hydrogenated to the amine.<sup>5</sup> The azide was an oil which was taken up in ether and distilled at 92° at 0.9 mm.

ANAL. Calcd. for  $C_7H_7ON_3$ : N, 28.2%. Found: N, 28.6%.

*β-(4-Azidophenoxy)ethanol.* *β*-(4-Aminophenoxy)ethanol was converted to the azide.<sup>6</sup> Following recrystallization from a benzene–hexane mixture at ice temperature, the product melted at 37–38°.

ANAL. Calcd. for  $C_8H_9O_2N_3$ : N, 23.4%. Found: N, 22.7%.

### Azide Polymers

*Azidophthalate of partially hydrolyzed poly(vinyl acetate).* To a solution of 29.5 g. (0.21 mole free hydroxyl) of 47 mole-% hydrolyzed, high-viscosity poly(vinyl acetate) (Elvanol RH-611, Du Pont) in 590 g. of dry pyridine

\* Melting points are corrected.

† Mr. F. Wanamaker and Dr. L. Weisler determined the ratio of the isomers on the polymer by the 6.82  $\mu$  absorption band of the 3 isomer.

was added 39.5 g. (0.21 mole) of azidophthalic anhydride. The solution was heated, with stirring, for 5 hr. at 45–50° and allowed to stand overnight at room temperature. After dilution with 150 ml. of acetone, the mixture was poured slowly, with vigorous stirring, into 15 l. of 2.5% hydrochloric acid. The fine, white, fibrous polymer (60 g.) which precipitated was washed in three changes of fresh water and dried at 40°. It was soluble in acetone, dioxane, and dilute aqueous alkali.

ANAL. Calcd. for 100% reaction: N, 12.8%. Found: N, 10.8%.

*Azidobenzoate of partially hydrolyzed poly(vinyl acetate).* This polymer was made in the same manner and with the same materials as the polymer just described, except that *p*-azidobenzoyl chloride was used. After a 4-hr. heating period, the product was precipitated, then reprecipitated, in water. It was soluble in butanone and chloroform.

ANAL. Calcd. for 100% reaction: N, 14.2%. Found: N, 12.7%.

*Azidophthalate of partially hydrolyzed cellulose acetate.* A mixture of 10.1 g. (0.053 mole) of 3-azidophthalic anhydride and 6 g. (0.050 mole hydroxyl) of a partially hydrolyzed cellulose acetate (24% acetyl) in 80 ml. of pyridine was stirred at room temperature for 18 hr. Dilution with 50 ml. of butanone gave the proper concentration for precipitation in methanol. The product was washed in dilute acetic acid and then in water. It was soluble in dilute aqueous alkali.

ANAL. Calcd. for 100% reaction: N, 13.0%. Found: N, 11.7%.

*3-Azidophthalate of gelatin.* A solution of 10 g. (about 0.004 mole of free amino) of gelatin in 110 ml. of water was stirred at 50° while 5 g. (0.026 mole) of 3-azidophthalic anhydride was added in small portions along with sufficient 10% sodium hydroxide to maintain the pH at 8–10. Heating was continued for 3 hr., after which the solution was acidified with acetic acid to pH 6. The polymer, recovered by precipitation in acetone, was soluble in alkali.

*Esterification of styrene-maleic anhydride heteropolymer with m-azidobenzyl alcohol.* To a solution of 8.1 g. (0.040 mole) of styrene-maleic anhydride heteropolymer (inherent viscosity, 0.5 in acetone, 0.25 g./100 ml.) in 130 ml. of dry pyridine was added 4.0 g. (0.027 mole) of *m*-azidobenzyl alcohol. The solution was maintained at 70° for 4 hr. and allowed to stand overnight at room temperature. The polymer was precipitated in ethyl ether and reprecipitated from 250 ml. of acetone in 0.3% hydrochloric acid. The washed and dried polymer was soluble in dilute aqueous alkali. A nitrogen content of 5.7% indicates that 36% of the maleic anhydride units were esterified.

*Esterification of styrene-maleic anhydride heteropolymer with  $\beta$ -(4-azidophenoxy)ethanol.* A 13-g. amount (0.064 mole) of styrene-maleic anhydride was treated with 10 g. (0.056 mole) of this azide as just described. Esterification was 55% as determined by a nitrogen content of 7.5%. The polymer was soluble in dilute aqueous alkali containing 10% ethanol.

*Examination of Light Sensitivity of the Polymers*

The method of measuring the photoreactivity of a polymer has been described.<sup>7,8</sup> This procedure was followed in our work, with minor variations. The photographic speed value  $S$  (sensitivity value in the work cited) of the polymers is defined as the reciprocal of the exposure required to insolubilize the polymer which has been coated on a silicated aluminum sheet. To measure the exposure, a neutral-density filter is placed against the coating, and the transmitted illuminance is inversely proportional to the antilog of the photographic density  $D$  of the filter. The speed values were calculated in terms of a control speed value from the equation

$$S_x = S_c \frac{\text{antilog } D_x}{\text{antilog } D_c}$$

where the subscripts  $X$  and  $c$  refer to the sample and control, respectively. Poly(vinyl cinnamate) with a speed of 2.2 was the control.<sup>7</sup>

Sensitizers, when used, were included in the coating solutions at the level of 10% of the weight of the polymer.

**RESULTS AND DISCUSSION**

Table I gives the speed values and sensitized speed values of the photo-reactive azide polymers. The data show that the speed has no direct relationship to the azide nitrogen content. Furthermore, poly(vinyl acetate 3-, 4-azidophthalate) samples with nitrogen contents in the range of 9.5–11.5% showed random variations in speed of 35–120 which were apparently dependent on factors other than azide content.

The measured speed of the photoreaction will be a function of the cross-links and thus of the solubility of the exposed polymer. Too, it will be a function of factors which are external to the actual crosslinking. The speed is a measure of the minimum exposure which will leave a layer of polymer adhered to the substrate after development. Coating thickness and adhesion of the insolubilized polymer are two factors which affect the measurement.

The crosslinking reaction is subject to variations which depend on organic structure. One is the actual amount of energy necessary to decompose an azide group. Related to that is the ability of the molecule to utilize the energy of the incident radiation. Exposure through a high-silica glass essentially limits the spectrum to wavelengths above 260  $m\mu$ . The azides all have comparable absorption peaks and ranges. Variations of 10  $m\mu$  are not significant as they are not reproducible. The narrow range of poly(vinyl cinnamate) partly accounts for its lower sensitivity.

The principal function of sensitizers is to extend the absorption range into the region of longer wavelengths. As shown by the table, this is done by the two sensitizers, one of which is alkali-soluble and the other organic-soluble. With the azidophthalates the sensitizer uniformly increases speed by a factor of five, and it adds another absorption peak at longer wave-

TABLE I  
Sensitivity and Spectral Response of Azide Polymers

Polymer	Azide N, %	Coating solvent	Speed value	Sensi- tized speed value	Unsensitized absorption		Sensitized absorption	
					$E_{max}$ , m $\mu$	Range, m $\mu$	$E_{max}$ , m $\mu$	Range, m $\mu$
Control, poly(vinyl cinnamate)		Cyclohexanone	2.2		310	260-340		
Poly(vinyl acetate 3-azidophthalate)	10.8	0.5% NH <sub>3</sub>	50	250 <sup>b</sup>	310	270-390	310; 410	270-460
Poly(vinyl acetate 4-azidophthalate)	9.7	0.5% NH <sub>3</sub>	220	1100 <sup>b</sup>	310	260-380	310; 420	270-450
Poly(vinyl acetate 3-, 4-azidophthalate)	10.5	0.5% NH <sub>3</sub>	100	440 <sup>b</sup>	320	270-390	320; 420	270-460
Poly(vinyl acetate <i>p</i> -azidobenzoate)	12.7	Cyclohexanone	110	3100 <sup>c</sup>	310	270-390	310; 410	270-450
Cellulose acetate 3-azidophthalate	11.7	0.5% NH <sub>3</sub>	9	12 <sup>c</sup>	320	290-350		
Gelatin 3-azidophthalamide	(1.5) <sup>a</sup>	0.5% NH <sub>3</sub>	9	18 <sup>c</sup>	(flat)	290-370		
Styrene-MA ester of <i>m</i> -azidobenzyl alcohol	5.7	0.5% NH <sub>3</sub>	35		(flat)	280-370		
Styrene-MA ester of 3-(4-azidophenoxy)eth- anol	7.5	0.5% NH <sub>3</sub> + 10% EtOH	120		310;	280-400		
					350			

<sup>a</sup> Maximum possible is 1.5, based on free amine content of gelatin; azide N was not measured.

<sup>b</sup> Sensitizer: 2-(3-sulfobenzoylmethylene)-1-methyl- $\beta$ -naphthothiazoline.

<sup>c</sup> Sensitizer: 2-Benzoylmethylene-1-methyl- $\beta$ -naphthothiazoline.

lengths. The remarkable sensitization of the poly(vinyl acetate azidobenzoate) is unique among the azides. The mechanism of this response is not known.

Studies reported in the literature<sup>9,10</sup> on the thermal decomposition of organic azides show that the decomposition is unimolecular and the rate is independent of the solvent, except for some catalysis by strong acid.<sup>1</sup> Photochemical decomposition has given the same products when the two processes have been compared.<sup>1,11</sup> The thermal and photochemical reactions are probably comparable in mechanism. The rate-determining step is the loss of nitrogen, and the fate of the imine radical is a function of its environment. For example, in the presence of alkylbenzene, the decomposition product of phenyl azide abstracts hydrogen from the side chain of the solvent. In the presence of benzene, the imine radical will combine with another of its kind in preference to abstraction of nuclear hydrogen.<sup>12</sup> This correlates with work we have done<sup>13</sup> in crosslinking polymers by irradiation in the presence of simple bisazides. Polyvinyltoluene was more rapidly insolubilized than was polystyrene.

A few experiments on the irradiation of aromatic azides without solvent to simulate conditions of a polymer coating indicated how diverse the reaction can be, depending on the molecules involved.<sup>13</sup> When irradiated in the crystal form, *p*-azidobenzoic acid gave *p,p'*-dicarboxyazobenzene. Phenyl azide, irradiated in air, gave an amorphous solid with the empirical formula  $C_6H_6ON$ . Irradiation of phenyl azide in a nitrogen atmosphere gave another unidentifiable product,  $C_6H_7N$ . In neither case was azobenzene formed. The significance of these facts is that the rate of photochemical decomposition of a given azide will not be changed by altering the material with which the imine radical eventually reacts, but the fate of that radical and its efficient utilization (e.g., insolubilization of a polymer) can be controlled by the nature of the other groups in the system.

From the azide polymers described here, little can be stated about the effectiveness of various groups in increasing the observed photoreactivity. The 4 isomer of the azidophthalate shows a pronounced speed increase over the 3 isomer. Perhaps less energy is required to decompose the 4 azido isomer, or that imine radical, for steric reasons, is more efficient in crosslinking in competition with an intramolecular reaction than is the 3 isomer. The poly(vinyl acetate) derivatives have higher speeds than the other polymers. This might suggest that the acetate group is particularly effective as a crosslinking site but the cellulose acetate derivative is a low-speed polymer with a high azide content. For its azide content, the gelatin derivative has a high speed. Since gelatin is insoluble in cold water, the small amount of carboxyl group contributed by the azidophthalamide may give it only marginal solubility in alkali. Even lightly crosslinked polymer would then be insoluble in the developer. The two azide polymers derived from styrene-maleic acid copolymer have different light sensitivities, presumably because of the difference of the two aryl azide groups.

To separate the factors which cause speed variations in photoreactive

azide polymers, the photoreaction must be isolated from the subsequent coupling reaction. The quantum efficiency of decomposition of substituted aryl azides should be known independently of the ability of various groups to couple with the imine radical.

We wish to acknowledge the contribution of Mr. E. M. Robertson and his co-workers who determined the light sensitivity data.

### References

1. Smith, P. A. S., and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2435, 2438 (1951).
2. Smith, P. A. S., B. B. Brown, R. K. Putney, and R. F. Reinisch, *J. Am. Chem. Soc.*, **75**, 6335 (1953).
3. Merrill, S. H., *J. Org. Chem.*, **25**, 1882 (1960).
4. Griess, P., *Z. für Chem.*, 165 (1867).
5. Phillips, A. P., and A. Maggiolo, *J. Org. Chem.*, **15**, 659 (1950).
6. Sukis, A. J., and R. C. Tallman, *J. Am. Chem. Soc.*, **66**, 1461 (1944).
7. Minsk, L. M., J. G. Smith, W. P. VanDeusen, and J. F. Wright, *J. Appl. Polymer Sci.*, **2**, 302 (1959).
8. Robertson, E. M., W. P. VanDeusen, and L. M. Minsk, *ibid.*, **2**, 308 (1959).
9. Russell, K. E., *J. Am. Chem. Soc.*, **77**, 3487 (1955).
10. Fagley, T. F., J. R. Sutter, and R. L. Oglukian, *J. Am. Chem. Soc.*, **78**, 5567 (1956).
11. Kirmse, W., *Angew. Chem.*, **71**, 537 (1959).
12. Bertho, A., *Ber.*, **57**, 1138 (1924).
13. Merrill, S. H., and C. C. Unruh, unpublished work.

### Synopsis

Derivatives of poly(vinyl alcohol), styrene-maleic acid copolymer, cellulose, and gelatin have been made which incorporate aromatic azide groups into the polymer molecule. The relative rates at which these polymers become crosslinked on exposure to ultraviolet light were measured. A preliminary discussion is given of the structural factors involved in the photolytic decomposition and subsequent coupling reaction.

### Résumé

On a préparé des dérivés de l'alcool polyvinylique, du copolymère styrène-acide maléique, de la cellulose et de la gélatine qui contiennent des groupements acides aromatiques dans la molécule du polymère. Ces polymères ont été exposés à la lumière et les vitesses relatives avec lesquelles ils sont pontés ont été mesurées. On ajoute une discussion préliminaire sur les facteurs structurels impliqués dans la décomposition photolytique et la réaction de couplage qui s'en suit.

### Zusammenfassung

Derivate von Polyvinylalkohol, Styrol-Maleinsäurecopolymeren, Cellulose und Gelatine mit eingebauten aromatischen Azidgruppen in der Polymermolekel wurden dargestellt. Die relative Vernetzungsgeschwindigkeit dieser Polymeren im ultravioletten Licht wurden gemessen. Eine vorläufige Diskussion der bei der photolytischen Zersetzung und darauf folgenden Kupplungsreaktion wirksamen strukturellen Einflüsse wird durchgeführt.

Received October 31, 1961