

tion from isoamyl ether and diethyl ether there was obtained 1.16 g. melting at 235–236°.

*Anal.* Calcd. for  $C_{38}H_{31}NO$ : C, 87.59; H, 6.33; N, 2.83. Found: C, 88.37; H, 6.15; N, 2.83.

**Decomposition of 2,4,6-Triphenyl-2,3,4,5-tetrahydropyridyl-3-diphenylcarbinol.**—A mixture of 1.50 g. (0.0030 mole) of 2,4,6-triphenyl-2,3,4,5-tetrahydropyridyl-3-diphenylcarbinol with 1.00 g. (0.031 g. atom) of sulfur was heated at about 300° for one hour. From the reaction mixture was obtained by vacuum distillation 0.33 g., 0.0018 mole (60%) of benzophenone which was identified by mixed melting point and by preparation of the 2,4-dinitrophenylhydrazone. From the distillation residue was obtained 1.01 g. of 2,4,6-triphenylpyridine contaminated with benzophenone. After two crystallizations from ethanol there was obtained 0.69 g., 0.0024 mole (75%) of 2,4,6-triphenylpyridine which was identified by mixed melting point and by preparation of the picrate.

**2,4,6-Triphenyl-3-benzoylpyridine.**—A mixture of 1.00 g. (0.0024 mole) of V and 2.00 g. (0.062 g. atom) of sulfur was heated for two hours until no more hydrogen sulfide was evolved. The product in the flask was extracted with six portions, each 50 cc., of boiling methanol. The extract was distilled to a volume of 30 cc. and after having stood for twenty-four hours deposited 0.92 g., 0.0022 mole (92%) of 2,4,6-triphenyl-3-benzoylpyridine melting at 157–160°. This material was freed from sulfur by stirring it in acetone solution with mercury. After several crystallizations from ethanol it melted at 169.0–169.5°.

*Anal.* Calcd. for  $C_{30}H_{21}NO$ : C, 87.56; H, 5.14; N, 3.40. Found: C, 87.53; H, 5.20; N, 3.34.

### Summary

The dimer of styryl phenyl ketimine produced by neutral hydrolysis of the Grignard addition product from phenylmagnesium bromide and styryl cyanide has been found by degradation methods to be 2,4,6-triphenyl-2,5-endo-(2'-phenylethylene)-2,3,4,5-tetrahydropyrimidine.

The product from the pyrolysis of this compound with sulfur is 2,4,6-triphenylpyrimidine. When phenylcyanoacetylene is treated with phenylmagnesium bromide, 2,4,6-triphenylpyrimidine is obtained rather than 2,4,6-triphenyl-2,5-endo-(2'-phenylacetylene)-2,3-dihydropyrimidine. Since the latter would be expected to be unstable, this indicates that the reaction series may be typical for  $\alpha,\beta$ -unsaturated ketimines.

The acid hydrolysis of 2,4,6-triphenyl-2,5-endo-(2'-phenylethylene)-2,3,4,5-tetrahydropyrimidine leads to 2,4,6-triphenyl-3-benzoyl-2,3,4,5-tetrahydropyridine. The reactions of this compound with Grignard reagents are normal and substantiate the original proof of structure, but the reaction with benzoyl chloride involves an abnormality which may be typical of tetrahydropyridines.

TORONTO, ONTARIO

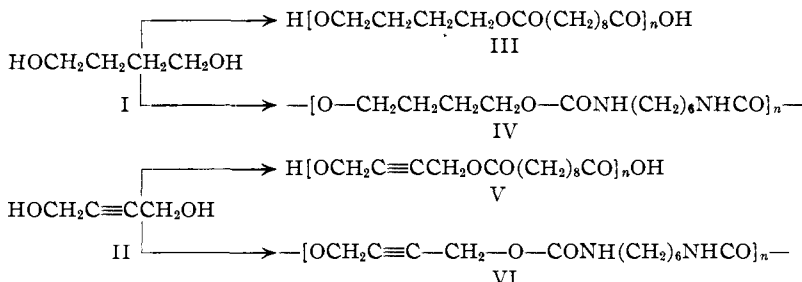
RECEIVED SEPTEMBER 22, 1949

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Effect of an Acetylenic Unit on the Physical Properties of Polyesters and Polyurethans

BY C. S. MARVEL AND JOHN H. JOHNSON<sup>1</sup>

In order to learn what change in the physical properties of a polymer is produced when a regularly recurring  $-CH_2CH_2-$  unit is replaced by a  $-C\equiv C-$  unit, we have synthesized the polysebacates and the polyurethans from hexamethylene diisocyanate with butane-1,4-diol (I) and with 2-butyne-1,4-diol (II).



The polytetramethylene sebacate (III) was prepared readily by standard ester interchange technique<sup>2</sup> from the glycol and dimethyl sebacate with litharge as the catalyst.<sup>3</sup> When the same procedure was tried with 2-butyne-1,4-diol, an

(1) Allied Chemical and Dye Corporation Fellow, 1948–1949.

(2) (a) Carothers and Arvin, *THIS JOURNAL*, **51**, 2560 (1929);

(b) Hardy, *J. Soc. Chem. Ind.*, **67**, 426 (1948).

(3) Harber and Yoran, *Ind. Eng. Chem.*, **37**, 953 (1945).

insoluble polyester was obtained due to some secondary reactions which appeared to involve the triple bond. A low molecular weight soluble polyester was obtained from the acetylenic glycol in the ester interchange reaction when barium oxide was used as a catalyst. Direct esterification of the glycol by heating with sebacic acid appeared to be better than ester interchange as a method of preparing the acetylenic polyester. The intrinsic viscosity of the highest molecular weight acetylenic polyester which was obtained was 0.19, so the saturated ester was prepared with approximately the same intrinsic viscosity (0.26) in order that polymers of nearly equal size could be compared.

The polyurethans (IV and VI) were prepared from the glycols (I and II) and hexamethylene diisocyanate in chlorobenzene solution by the method used by Baeyer<sup>4</sup> for this type of polymer. Baeyer has described the polyurethans from tetramethylene glycol, but since his paper is not

(4) Otto Baeyer, private communication, 1947; B. I. O. S. Final Reports 1947 and 1948; C. I. O. S. Report File No. XXIX-12 (Appendix); U. S. Patent 2,343,808 (1944); C. A., **38**, 3393 (1944).

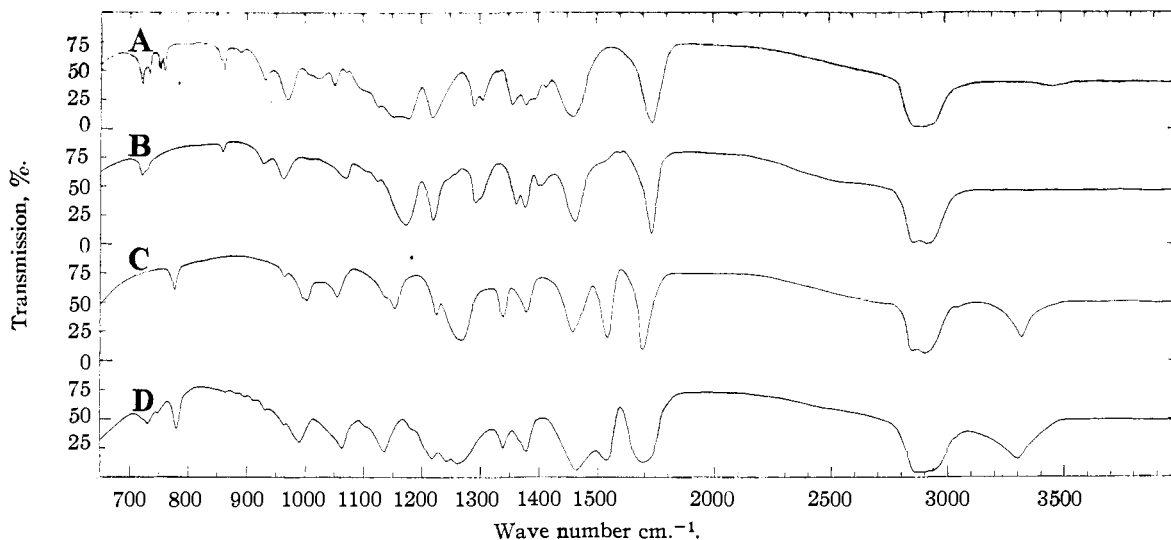


Fig. 1.—Infrared absorption curves of polyesters and polyurethans: A, polyester from 1,4-butynediol; B, polyester from 1,4-butanediol; C, polyurethan from 1,4-butynediol; D, polyurethan from 1,4-butanediol.

readily accessible, we have reported details on our experiments. The acetylenic glycol gave a soluble polyurethan with an intrinsic viscosity of 0.23 and hence a saturated polyurethan of approximately the same viscosity (0.25) was prepared for comparison.

Copolymers of butane-1,4-diol and 2-butyne-1,4-diol with hexamethylene diisocyanate containing the glycol in the ratio of 80:20 and 20:80 parts, respectively, were also prepared in order that Flory's<sup>5</sup> method of determining the heat and entropy of fusion by measuring melting point depressions could be applied to these polymers.

All of the polymers were characterized by determining their infrared absorption curves<sup>6</sup> and these are recorded in Fig. 1.

All of the polymers gave the expected carbonyl bands at 1700  $\text{cm}^{-1}$ . The polyurethans gave the amide bands at 1530 and 3300  $\text{cm}^{-1}$ . The expected bands for a  $-\text{C}\equiv\text{C}-$  in the acetylenic polymers were very weak in the polyurethans and apparently not discernible in the polyester curves. 2-Butyne-1,4-diol itself gave a very weak band at 2113  $\text{cm}^{-1}$  and in its polyurethan there is a slight amount of absorption at 2114  $\text{cm}^{-1}$ . Apparently this band is almost lost in the polymers by some dilution effect. This has been observed in simpler acetylenic derivatives.<sup>7</sup>

For further characterization of the polymers X-ray powder diffraction patterns were determined with a Norelco X-ray spectrometer using copper  $K\alpha$  radiation.<sup>8</sup> The results are recorded in Table I and Figs. 2 and 3.

(5) Flory, *J. Chem. Phys.*, **15**, 685 (1947).

(6) We are indebted to Miss Elizabeth M. Peterson for the infrared absorption curves and their interpretation.

(7) F. A. Miller, private communication.

(8) We are indebted to Professor G. L. Clark and Mr. R. S. Sprague for these X-ray data.

| Saturated                           |               | Unsaturated            |               |
|-------------------------------------|---------------|------------------------|---------------|
| Peak angle, <sup>a</sup><br>degrees | d Spacing, Å. | Peak angle,<br>degrees | d Spacing, Å. |
| Polyesters                          |               |                        |               |
| ..                                  | ..            | 12.3                   | 7.18          |
| 19.9                                | 4.46          | 19.1                   | 4.64          |
| 21.5                                | 4.13          | 21.8                   | 4.07          |
| 23.7                                | 3.75          | 24.4                   | 3.64          |
| Polyurethans                        |               |                        |               |
| ..                                  | ..            | 9.5                    | 9.29          |
| 21.0                                | 4.22          | 20.9                   | 4.24          |
| ..                                  | ..            | 21.7                   | 4.09          |
| 24.2                                | 3.67          | 25.3                   | 3.52          |

<sup>a</sup> The peak angle is  $2\theta$  or two times the angle of diffraction.

These patterns indicate the expected high degree of regularity in these condensation polymers.

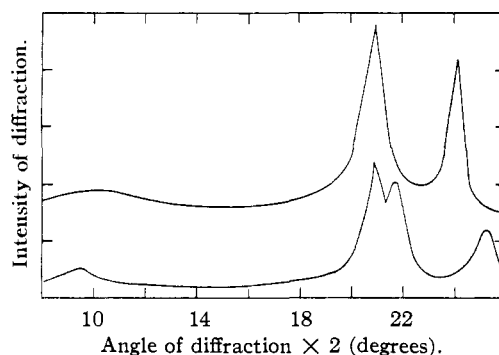


Fig. 2.—X-Ray diffraction patterns of polyesters: upper curve, polysebacate of 1,4-butanediol; lower curve, polysebacate of 1,4-butynediol.

Since we were particularly interested in the low temperature behavior of the polymers containing

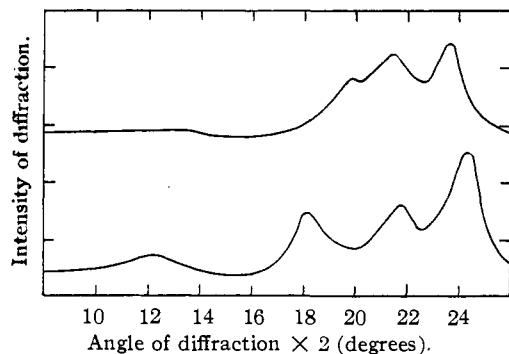


Fig. 3.—X-Ray diffraction patterns of polyurethans: upper curve, polyurethan from 1,4-butanediol; lower curve, polyurethan from 1,4-butyne-1,3-diol.

triple bonds, we have determined the second order transition temperatures (sometimes called the internal melting points of polymers) of the polyesters and polyurethans according to the procedure of Bekkedahl.<sup>9</sup> These are reported in Table II.

TABLE II  
SECOND ORDER TRANSITION TEMPERATURES OF POLYESTERS AND POLYURETHANS

| Polymer                          | Intrinsic viscosity | Capillary temp., °C., m. p. | Second order transition temp., °C. |
|----------------------------------|---------------------|-----------------------------|------------------------------------|
| Polyesters of butane-1,4-diol    | 0.98                | 64-65                       | -75                                |
| Polyester of butane-1,4-diol     | .26                 | 64-64.5                     | -57                                |
| Polyester of 2-butyne-1,4-diol   | .19                 | 51-53                       | -27                                |
| Polyester of 2-butyne-1,4-diol   | .20                 | 51-53                       | -26                                |
| Polyurethan of butane-1,4-diol   | .25                 | 176-177                     | -58                                |
| Polyurethan of 2-butyne-1,4-diol | .23                 | 149-150                     | -45                                |

\* All melting points reported in this manuscript have been corrected for stem exposure.

It is interesting to note that whereas the capillary melting points of the saturated polymers are always higher than those of the acetylenic polymers, the reverse is true for the second order transition temperatures. Thus the saturated polymers retain their amorphous areas at lower temperatures than do their counterparts with acetylenic unsaturation.

The data on the polyurethans which were measured and calculated from the Flory formula<sup>5</sup> are recorded in Table III.

TABLE III  
PHYSICAL CONSTANTS AND THERMODYNAMIC VALUES FOR POLYURETHANS OF BUTANE-1,4-DIOL AND 2-BUTYNE-1,4-DIOL AND MIXTURES

| Polyurethan, satd.-unsatd. | Intrinsic viscosity | Value used for melting point, °C. | Calcd. heat of fusion, cal. | Calcd. entropy of fusion, cal./deg. |
|----------------------------|---------------------|-----------------------------------|-----------------------------|-------------------------------------|
| 100-0                      | 0.17                | 175                               | 7000                        | 15.7                                |
| 80-20                      | .17                 | 163                               | ..                          | ..                                  |
| 20-80                      | .19                 | 128                               | ..                          | ..                                  |
| 0-100                      | .17                 | 146                               | 4000                        | 10                                  |

(9) Bekkedahl, *J. Research Natl. Bur. Standards*, **13**, 411 (1934).

These data indicate that the acetylenic polymers are stiffer than the corresponding saturated polymers. This is in agreement with the results of second order transition temperature measurements. It is thus evident that introduction of acetylenic residues in place of a saturated residue makes such polymers less satisfactory for low temperature uses.

We are indebted to Dr. Carl E. Black III for helpful discussions in connection with this work.

### Experimental

**Polyesters.**—The apparatus used was that described by Hardy.<sup>2b</sup> The transesterifications were done in an oxygen-free nitrogen atmosphere. Especial care was required when 2-butyne-1,4-diol was used in order to avoid insolubilization of the polymers.

The bath temperatures of 100° were obtained by steam; of 142° by di-*n*-butyl ether vapors; of 172° by phenetol vapors; of 215° by 1,3,5-triethylbenzene vapors; and of 259° by diphenyl ether vapors. The yields of polyester were in the range of 90% of the theoretical.

**Polytetramethylene Sebacate.**—To a mixture of 4.95 g. (0.055 mole) of butane-1,4-diol and 11.5 g. (0.05 mole) of dimethyl sebacate was added 0.1 g. of litharge, and the mixture was heated at 183° for two hours at atmospheric pressure; then the temperature was raised to 259° and the pressure lowered to 0.01 mm. rather rapidly. The melt became highly viscous. After thirty minutes the reaction was discontinued, and the polymer was isolated and purified by solution in 100 cc. of hot chloroform, filtration and subsequent precipitation by addition of just enough acetone (usually 100 cc.) so the polyester separated when the mixture was cooled.

The ester melted at 64-64.5° and had an intrinsic viscosity of 0.61 (measured on a 0.4% solution in chloroform at 25.5°). Both the crude and purified polyesters could be cold drawn to give fibers.

*Anal.*<sup>10</sup> Calcd. for C<sub>14</sub>H<sub>24</sub>O<sub>4</sub>: C, 65.60; H, 9.44. Found: C, 65.73; H, 9.69.

When the same charge was used and heated to 155° at atmospheric pressure for three hours followed by one hour at this temperature and 0.03 mm. pressure, the purified ester had an intrinsic viscosity of 0.33, m. p. 64-64.5°. This ester did cold draw but gave weak fibers.

In another case 0.1 g. of di-*t*-butylhydroquinone was added to the same charge as an antioxidant. The mixture was heated for two hours at 172° at atmospheric pressure, then during four hours at this temperature the pressure was reduced to 0.05 mm. The temperature was then raised to 215° and the reaction mixture heated overnight. The resulting polymer was white but not sharp melting. It had an intrinsic viscosity of 1.16 and could be readily cold drawn into fibers.

In another run 0.1 g. of pyrophoric lead<sup>11</sup> was substituted for the 0.05 g. of litharge in the first experiment described. The reaction mixture was heated at 172° for two hours at atmospheric pressure. The pressure was reduced to 1 mm. over a period of six hours. The temperature was then raised to 215° and held at this point overnight with the pressure at 1 mm. The polymer was purified as before and had an intrinsic viscosity of 0.98 (see Table II).

The same charge of reagents was heated at 172° at atmospheric pressure for six to seven hours to yield a polymer of intrinsic viscosity of 0.26 (see Table II).

**Polysebacate of 2-Butyne-1,4-diol.**—A mixture of 4.95 g. of 2-butyne-1,4-diol,<sup>12</sup> 11.5 g. of dimethyl sebacate and

(10) Microanalyses reported in this paper were done by Miss Emily Davis and Miss Jane Wood and by the Clark Microanalytical Laboratory, Urbana, Illinois.

(11) Marvel and Johnson, *THIS JOURNAL*, **72**, 624 (1950).

(12) We are indebted to the General Aniline and Film Corporation and the Electrochemical Department of E. I. du Pont de Nemours and Company for generous samples of 2-butyne-1,4-diol.

0.1 g. of litharge was heated at 100° under 2 mm. pressure for three hours and then at 142° for overnight. The melt was very dark. The polymer was purified as described for the saturated polymer, m. p. 49°,  $[\eta]$  0.08.

*Anal.* Calcd. for  $C_{14}H_{20}O_4$ : C, 66.64; H, 7.94. Found: C, 65.75; H, 8.64.

The same quantities of glycol and sebacic ester, to which had been added 0.1 g. of barium oxide and 0.1 g. of di-*t*-butylhydroquinone, were heated at 185° for eight hours at atmospheric pressure and then overnight at 0.04 mm. pressure. A light colored polymer, m. p. 51–53°,  $[\eta]$  0.12, was obtained.

*Anal.* Calcd. for  $C_{14}H_{20}O_4$ : C, 66.64; H, 7.94. Found: C, 66.44; H, 8.41.

A mixture of 4.95 g. of 2-butyne-1,4-diol and 10.1 g. of sebacic acid was heated at 172° under atmospheric pressure for two hours and then under a pressure of 0.04 mm. for an additional eighteen hours. The melt was purified as described before. The polymer thus obtained was slightly dark, but was soluble; m. p. 51–53°,  $[\eta]$  0.19 (Table II). The crude polymer would cold draw but the purified polymer would not, possibly because some degradation had occurred in processing it.

**Polyurethan from Butane-1,4-diol and 1,6-Hexamethylene Diisocyanate.**—A solution of 2.68 g. of butane-1,4-diol in 100 ml. of a mixture of 80 parts by volume of chlorobenzene and 20 parts by volume of *o*-dichlorobenzene was placed in a dry 3-l. flask, equipped with agitator, dropping funnel, inlet tube for nitrogen gas, and reflux condenser. The apparatus was swept out with dry oxygen-free nitrogen. The solution was heated to refluxing temperature and a solution of 5 g. of hexamethylene diisocyanate in 50 ml. of the solvent was added from the dropping funnel. About half of the isocyanate solution was added quickly to the well-stirred glycol solution, and the remainder was added over a period of three to four hours. The solution was held at reflux temperature for about an hour after the solution of diisocyanate had all been added.

On cooling the mixture to room temperature the polymer precipitated and the solvent was decanted. The polymer was dissolved in 50 ml. of hot dimethylformamide and the solution filtered while hot. To the warm solution 50 ml. of methanol was added. The clear solution was allowed to stand overnight in a refrigerator. The polymer which separated was collected on a filter and dried overnight at room temperature and 0.1 mm. pressure. The intrinsic viscosity was determined on a 0.4% solution in *m*-cresol at 25.5°, m. p. 175–176°,  $[\eta]$  0.7.

*Anal.* Calcd. for  $C_{12}H_{22}N_2O_4$ : C, 55.80; H, 8.59; N, 10.84. Found: C, 55.81; H, 8.57; N, 10.73.

A run made with only chlorobenzene as a solvent gave a polymer, m. p. 174–175°,  $[\eta]$  0.17 (Table III).

A run made with 8 g. of glycol and 15 g. of diisocyanate in chlorobenzene gave 20 g. of polymer (87% yield), m. p. 176–177°,  $[\eta]$  0.25 (Table II).

**Polyurethan from 2-Butyne-1,4-diol and 1,6-Hexamethylene Diisocyanate.**—From 2.56 g. of 2-butyne-1,4-diol and 5 g. of hexamethylene diisocyanate in mixed chlorobenzene-*o*-dichlorobenzene solvent under the conditions described for the saturated glycol, there was obtained, upon purification, a polyurethan, m. p. 149–150°,  $[\eta]$  0.23 (Table III).

*Anal.* Calcd. for  $C_{12}H_{18}N_2O_4$ : C, 56.68; H, 7.14; N, 11.01. Found: C, 56.48; H, 7.27; N, 11.00.

When chlorobenzene alone was used as a solvent, a polyurethan was obtained, m. p. 145–146°,  $[\eta]$  0.17 (Table III).

**Mixed Polyurethans.**—Under the same general conditions used for preparing the polyurethans from the pure glycols, a polymer was prepared from a mixture of 0.536 g. of butane-1,4-diol and 2.05 g. of 2-butyne-1,4-diol with 5 g. of hexamethylene diisocyanate. The yield of polymer was about 80% of the theoretical amount, m. p. 127–128°,  $[\eta]$  0.19.

*Anal.* Found: C, 56.28; H, 8.01; N, 10.65.

To obtain a copolymer containing the lower percentage of 2-butyne-1,4-diol, it was necessary to use slightly different conditions since the unsaturated diol seemed to react more sluggishly than the saturated diol. A mixture of 0.50 g. of 2-butyne-1,4-diol and 0.584 g. of butane-1,4-diol was heated with 5 g. of hexamethylene diisocyanate under the usual conditions for about a half hour, and then an additional 1.756 g. of butane-1,4-diol was added and the reaction was completed. The yield of purified copolymer was 75% of the theoretical amount, m. p. 161–163°,  $[\eta]$  0.17.

*Anal.* Found: C, 56.02; H, 8.49; N, 10.96.<sup>13</sup>

**Second Order Transition Temperature Determinations.**—The method of Bekkedahl<sup>9</sup> was followed. Ten to 15-g. samples of polymer were used with purified isoöctane as the confining liquid. The capillary scale readings were plotted against the temperature as measured by a thermocouple without determining absolute volume changes. Therefore, the measurements may be in error by a few degrees, but the general order of the values is undoubtedly correct.

**Heat and Entropy of Fusion of Polyurethans.**—The melting points used were ordinary capillary melting points and these may not represent the precise value for the disappearance of crystallinity. Also there is some difference in molecular weights of the samples as judged by their intrinsic viscosity, and this introduces a slight element of doubt on exact comparison, but the order of magnitude is the important point in this work.

### Summary

The polysebacates of butane-1,4-diol and of 2-butyne-1,4-diol and also the polyurethans of these two glycols with hexamethylene diisocyanate have been characterized.

The saturated esters and urethans have higher capillary melting points but lower second order transition points than do the polymers with the recurring acetylenic unit in the polymer chain. The saturated polyurethans have higher calculated heats of fusion and higher entropies of fusion than do the polymers containing the acetylenic structure.

URBANA, ILLINOIS

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(13) We are indebted to Mr. Charles H. Young for this preparation.