spectra of isotopic molecules, particularly of deutero compounds when they are available, are valuable aids in the interpretation of infrared data.

The compound D_2NOD has not been reported in the literature. The usual method for the preparation of H_2NOH involves the neutralization of hydroxyammonium chloride by sodium butoxide in a hydrogen-rich solvent such as butanol.[2] This is obviously not suited for the preparation of D_2NOD using reasonable amounts of D_2O. Moreover, our attempts to make D_2NOD by successive exchanges of H_2NOH with D_2O have been unsuccessful. It appears that a stable hydrate is formed which makes it impossible to recover the exchange water from the mixture, H_2NOH-H_2O, by a vacuum distillation. Another method of preparation of D_2NOD was attempted and proved to be successful. Uhlenhuth,[3] in 1900, prepared free hydroxylamine by the thermal decomposition of tertiary hydroxylammonium phosphate at reduced pressure. We have prepared H_2NOH by a modification of this procedure, which, when followed by two or three fractional sublimations resulted in a product melting at 32–33°, the same as that ascribed to pure hydroxylamine. Infrared spectra of this material in the region 500–4000 cm.$^{-1}$ were identical with those of H_2NOH prepared in the usual manner.

This method was adapted to the preparation of D_2NOD. The salt $(H_3NOH)_3PO_4$ was first converted to $(D_3NOD)_3PO_4$ by exchange with heavy water and this was followed by thermal decomposition to D_2NOD. The material was collected in a tube in the vacuum system, fractionally sublimed, and finally sublimed onto the rocksalt sample support of an infrared low-temperature cell.[4] In addition to offering a simple method for the preparation of D_2NOD using small amounts of D_2O, this method also has some obvious advantages for the preparation of small amounts of H_2NOH. A sample may be prepared and used on the same day. The melting point may be checked easily in the vacuum system by subliming a small amount into a capillary tube. All transfers are carried out *in vacuo*, thereby eliminating the danger of reaction with atmospheric vapors. Finally, the material may be conveniently purified by fractional sublimation.

Experimental Procedure

$(H_3NOH)_3PO_4$ was prepared by precipitation from a hot solution of H_3NOHCl and Na_3PO_4. This was filtered and dried in a vacuum desiccator over H_2SO_4.

For the preparation of D_2NOD, 0.7 g. $(H_3NOH)_3PO_4$ was introduced into a flask on the vacuum line. Enough D_2O (5.5 ml.) was added to dissolve the salt at 80°. The mixture was evaporated to dryness at reduced pressure and room temperature. The system was brought back to atmospheric pressure with dry nitrogen and a second portion of D_2O was added. Three more exchanges were made and the salt was finally dried by pumping at 0.015 mm. for several hours followed by a final heating to 110–120° at 13 mm. pressure.

The distillation of the D_2NOD from the salt was carried out at 13 mm. and 135–150°. Heating was done with a glycerol-bath which could be removed rapidly if necessary, and was carried out with the protection of a safety glass explosion screen. A bleeder valve between the pump and

the vacuum system was employed in order to add dry nitrogen to maintain the pressure at 13 mm. during distillation. Reaction began at about 130° at this pressure. The D_2NOD was collected in a portion of the apparatus at 0°. This material was fractionally sublimed into a tube at −80° and kept there until needed. Deutero-hydroxylamine prepared in this manner had a deuterium purity, as estimated from its infrared spectrum, of about 97%.

DEPARTMENT OF CHEMISTRY
STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON

The Melting Transition of Polymethylene[1]

By L. MANDELKERN, M. HELLMANN, D. W. BROWN, D. E. ROBERTS AND F. A. QUINN, JR.

Polymethylene, a linear polymeric hydrocarbon of high molecular weight, serves ideally as a model polymer in various physicochemical studies, because of the simplicity of its structure. It is particularly well suited for an investigation of the crystallization behavior of chain molecules, and in this connection we should like to present the results of a study of its volume–temperature behavior, and its melting temperature, T_m.

In Fig. 1, the relative volume of polymethylene (relative to that at 137°), as determined dilatometrically, is plotted as a function of temperature. A well defined first-order transition, or melting temperature, characterized by the disappearance of the last traces of crystallinity, occurs at 136.5 ± 0.5°, and 70% of the melting occurs in only a three to four degree interval. For comparative purposes similar data for a commercial sample of polyethylene, which is known to be highly branched,[2,3] are also plotted in Fig. 1. The melting temperature is lowered to 115° for the branched polymer and the melting range considerably extended in comparison with the linear one. The lowering of T_m and broadening of the melting range by branch units is in agreement with the predictions of the statistical equilibrium theory of crystallization in polymers.[4,5]

The melting temperature observed for polymethylene, 136 to 137°, is very close to the convergence temperature of 135° predicted for a high molecular weight *n*-paraffin by King and Garner[6] from an analysis of thermodynamic data for low molecular weight paraffins. This again illustrates the asymptotic relation between T_m and molecular weight in linear polymers.[4,5]

Recently a melting temperature of 132° has been reported[7] for a polymethylene prepared in a similar but not identical manner. This lower T_m may probably be attributed to the rapid heating rate (0.5°/min.) used in its determination. It has been

(1) The work reported here was supported by the Office of Naval Research and the Office of the Quartermaster General.

(2) R. B. Richards, *J. Applied Chem.*, **1**, 370 (1951).

(3) I. Harris, *J. Polymer Sci.*, **8**, 353 (1952).

(4) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

(5) R. D. Evans, H. R. Mighton and P. J. Flory, THIS JOURNAL, **72**, 2018 (1950).

(6) A. M. King and W. E. Garner, *J. Chem. Soc.*, 1449 (1934); 1368, 1372 (1936).

(7) S. W. Kantor and R. C. Osthoff, THIS JOURNAL, **75**, 931 (1953).

(2) C. D. Hurd, *Inorganic Syntheses*, **1**, 87 (1939).

(3) R. Uhlenhuth, *Ann.*, **311**, 117 (1900).

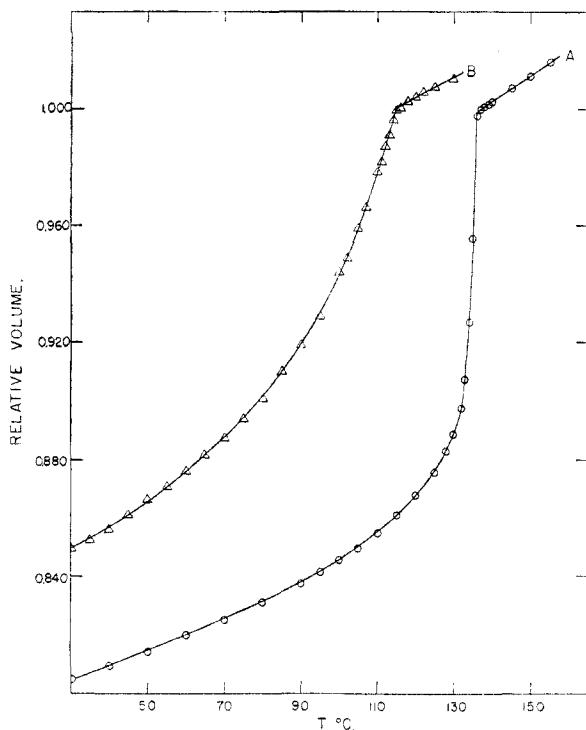(4) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950).

Fig. 1.—Relative volume–temperature curves: curve A for polymethylene O; curve B for polyethylene △.

demonstrated[5,8,9] that to obtain reliable values of T_m in polymers, the heating in the vicinity of the melting temperature must be gradual and should occur over a period of several days. Other observers[10,11] have reported the decomposition of polymethylene around 300° without noting any indication of melting at lower temperatures. If visual methods were employed, the true melting point was probably obscured by the very high viscosity of the polymer. Both the branched and linear polymers supercool, the amount of supercooling, of course, depending on the cooling rate.

Experimental.—Polymethylene was prepared according to the method described by Buckley and Ray[10] by means of the decomposition of diazomethane, using trimethyl borate as catalyst. The infrared absorption spectrum of thin films of the polymer was identical with that reported by these authors,[10] indicating the absence of methyl groups and hence a linear molecule. Its intrinsic viscosity in units of 100 ml./g., was 8.6 ± 0.1, in freshly distilled xylene at 100°, so that our polymer is of high molecular weight.[3] The polyethylene was obtained from the Bakelite Corporation and is designated as DYNH resin. Its physical properties have been described in the literature.[3]

The dilatometric samples were films approximately 0.2–0.3 mm. thick prepared from a 1% xylene solution held at 110° in an atmosphere of nitrogen at reduced pressure. After the bulk of the solvent was removed, the films were dried *in vacuo* at 70° for 28 hours. The dilatometric procedure, using mercury as a confining fluid, has been described previously.[8] Observations were made in the order of ascending temperature and in the melting region, the temperature was raised only 1° per 24 hours. A considerable amount of recrystallization, as has been observed in other polymers,[5,8,9] occurred.

National Bureau of Standards
Washington 25, D. C.

(8) P. J. Flory, L. Mandelkern and H. K. Hall, *ibid.*, **73**, 2352 (1951).
(9) L. Mandelkern, R. R. Garrett and P. J. Flory, *ibid.*, **74**, 3949 (1952).
(10) G. D. Buckley and N. H. Ray, *J. Chem. Soc.*, 3701 (1952).
(11) H. Meerwein, *Angew. Chem.*, **60**, 78 (1948).

cis- and trans-Propenylbenzene and their Azeotropes with n-Decane

By R. Y. Mixer,[1a] R. F. Heck,[1b] S. Winstein and William G. Young

Samples of pure *cis*- and *trans*-propenylbenzene were desired during the course of two independent investigations in these laboratories. The propenylbenzenes were needed as spectral standards for the infrared spectrographic analyses of olefins resulting from solvolysis of 2-phenyl-1-propyl and 1-phenyl-2-propyl *p*-bromobenzenesulfonates. They were also desired for testing azeotrope-formation with *n*-decane. These azeotropes were found during the distillation of the products from the reactions of sodium allylbenzene in pentane with methanol and various halides.[2]

Attempts to separate the pure *cis*-isomer from the propenylbenzenes obtained by isomerization of allylbenzene[3] were unsuccessful even though columns of *ca.* 100 theoretical plates were used. The propenylbenzene obtained in this manner was predominantly the *trans*-isomer.[4] Catalytic hydrogenation of 1-phenyl-1-propyne gave the *cis*-propenylbenzene which was satisfactorily purified by a precision distillation through a 112-theoretical-plate center-rod column. The *trans*-propenylbenzene was obtained without difficulty and free of the *cis*-isomer from the methanolysis of sodium allylbenzene in pentane. The small amount of the *cis*-isomer found in this reaction presumably was separated as the *n*-decane azeotrope.

Table I

PHYSICAL PROPERTIES AND ULTRAVIOLET ABSORPTION MAXIMA OF cis- AND trans-PROPENYLBENZENE

Isomer	cis	trans
B.p., °C. (20 mm.)	64.5	73.5
$n^{25}D$	1.5400	1.5473
d^{25}_4	0.9107	0.9019
MR_D, calcd.	39.69	39.69
found	40.69	41.56
exaltation	1.00	1.87

Ultraviolet absorption maxima in 95% ethanol

λ, mμ	ϵ_m	λ, mμ	ϵ_m
240.6	13800	250	17300
279	Shoulder	284	1100
290	120	293	780

The physical and optical properties of the *cis*- and *trans*-propenylbenzenes (Table I) clearly show the effects of steric inhibition of resonance in the *cis*-isomer due to interference between the ortho-hydrogen of the benzene ring and the methyl hydrogens in the side chain. This produces a reduction of 0.87 in the exaltation of the molecular refraction, and similar reductions are displayed by

(1) (a) Standard Oil Company of California Fellow in Chemistry 1950–1952; (b) research supported by Office of Naval Research.
(2) The results of these investigations are reported elsewhere.
(3) M. Tiffeneau, *Comp. rend.*, **139**, 482 (1904).
(4) The Am. Pet. Inst., "Selected Values of Properties of Hydrocarbons," Vol. III, Table 13p gives the following free energies of formation ($\Delta F°_{298}$ kcal.): *cis*-propenylbenzene, 51.84 and *trans*-propenylbenzene 51.08. From these values, the composition of the thermal equilibrium mixture is estimated to be 21.7% *cis*- and 78.3% *trans*-propenylbenzene.