

Thermodynamics of Crystallization in High Polymers III. Dependence of Melting Points of Polyesters on Molecular Weight and Composition

Robert D. Evans, Harold R. Mighton, and Paul J. Flory

Citation: The Journal of Chemical Physics 15, 685 (1947); doi: 10.1063/1.1746629

View online: http://dx.doi.org/10.1063/1.1746629

View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/15/9?ver=pdfcov

Published by the AIP Publishing

Articles you may be interested in

Molecular weight dependence of segmental alignment in a sheared polymer melt: A deuterium nuclear magnetic resonance investigation

J. Chem. Phys. **116**, 10020 (2002); 10.1063/1.1474577

Influence of molecular weight on the photorefractivity of polymer/liquid crystal composites Appl. Phys. Lett. **80**, 10 (2002); 10.1063/1.1427427

Dependence of the Elongational Behavior of Polystyrene Melts on Molecular Weight and Molecular Weight Distribution

J. Rheol. 24, 847 (1980); 10.1122/1.549587

Dilatometric Studies of High Polymers. II. Crystallization of Aromatic Polyesters

J. Appl. Phys. **20**, 571 (1949); 10.1063/1.1698427

Thermodynamics of Crystallization in High Polymers II. Simplified Derivation of MeltingPoint Relationships

J. Chem. Phys. 15, 684 (1947); 10.1063/1.1746627



Thermodynamics of Crystallization in High Polymers

III. Dependence of Melting Points of Polyesters on Molecular Weight and Composition^{1,2}

ROBERT D. EVANS, HAROLD R. MIGHTON, AND PAUL J. FLORY
The Goodyear Research Laboratory, Akron, Ohio
Iuly 24, 1947

A LTHOUGH fairly definite melting points have been assigned to a number of crystalline polymers and to a few copolymers, no adequate systematic study has been carried out either on the effects of molecular weight or on the influence of copolymer composition on the melting point. Recently we have undertaken in this laboratory a comprehensive investigation of the dependence of melting point and crystallinity on polymer constitution. Linear condensation polymers are especially well suited for this purpose and we have chosen the polyester, decamethylene adipate, for the preliminary experiments reported here.

Various copolymers have been prepared in which a portion of the decamethylene or the adipate residue is replaced by another glycol or dibasic acid radical. Decamethylene adipate polymers, varying in molecular weight and in the nature of the end groups have been prepared also. Melting points of these polymers and copolymers can be reproducibly measured using a micro-melting point apparatus, consisting of a low power microscope equipped with an electrically heated hot stage. The sample, located in the hot stage, is observed between crossed Polaroid sheets using transmitted light while the temperature is raised slowly. So long as crystallinity remains, the sample appears bright in a dark field. The fairly sharp disappearance of this manifestation of depolarization marks the "melting point," corresponding to complete disappearance of crystallinity.

The melting points of decamethylene adipate copolyesters in which 20-mole percent of the glycol or acid residues was replaced by the indicated comonomer residue, are presented in Table I. The same molar percentage of each of the first three comonomers lowers the melting point by the same amount in accordance with the theory presented in the preceding communication.³ The melting-point depression for the copolymer containing sebacate units, however, is appreciably less, indicating that the sebacate unit may occur within the crystallites.

When the proportion of the co-ingredient is varied, a plot of $1/T_m vs. \ln X_A$, where X_A is the mole fraction of decamethylene adipate units, is linear in agreement with theory.³ Eutectic compositions can be located in analogy with simple binary mixtures. From the slope of the $1/T_m vs. \ln X_A$ plot a heat of fusion of 3800 calories per decamethylene adipate unit is computed from Eq. (4) of the preceding paper.³

TABLE I. Melting points of decamethylene adipate copolyesters.

Comonomer group	η in poises at 218°C	m m, pt, (°C)
None	6800	81 -81.5
Isophthalate	600	64.5-65.5
cis-quinitol	310	66.5-67.5
Resorcinol	160	64 -65
Sebacate	770	72 -75

TABLE II. Effect of molecular weight on the melting point of decamethylene adipate.

\bar{x}_n	η in poises at 109°C	m m. pt. (°C)	m. pt. (°C) calc from Eq. (7)
2.5	0.171	42.5-45.5	45.3
5.05	0.616	62 -64	62.0
7.6	1.60	67 ~68	67.8
15.75	18.1	72.5-74	71.2
19.75	31.3	74 -75	74.0
85 est.	6800*	81 -81.5	80.0

^{*} Viscosity determined at 218°C.

The dependence of the melting point on the average number of structural units (the unit consisting of one decamethylene and one adipate radical) is shown in Table II for polymers terminated with benzoate groups. In agreement with Eqs. (5) and (6) of the preceding communication, 3 $1/T_m$ varies linearly with $1/\bar{x}_n$; i.e.,

$$1/T_m - 1/353 = 7.69 \times 10^{-4}/\bar{x}_n,\tag{7}$$

from which the melting points given in the last column of Table II have been computed. Comparing Eq. (7) with (6)³

$$h_u/(1+1/z) = 2600$$
 cal.,

which, in conjunction with the above value for h_u , leads to a not unreasonable value between 2 and 3 for z.

Decamethylene adipates having hydroxyl or carboxyl (or both) end groups, melt higher than benzoate terminated polymers of the same degree of polymerization. Occurrence of these smaller end groups within the crystal lattice affords a likely explanation for this observation.

We have concluded from these preliminary experiments that melting points of polymers depend in a systematic fashion on polymer constitution and that quantitative relationships can be traced. The results appear to be in accord with the theory outlined above.

¹ The work on which this paper is based comprises a part of a program of fundamental research on rubber and plastics being carried out under contract between the Office of Naval Research and the Goodyear Tire

and Rubber Company.

² Contribution No. 143 from the Goodyear Tire and Rubber Company, Research Laboratory.

³ See Paul J. Flory, J. Chem. Phys. 15, 684 (1947).

Resonance Energies from Thermal Data

T. L. COTTRELL AND L. E. SUTTON Physical Chemistry Laboratory, Oxford, England July 3, 1947

In a recent paper Dewart discussed the discrepancy between the values for resonance energies of benzene derivatives found by the Pauling-Sherman method from heats of combustion and by the Kistiakowsky method from heats of hydrogenation, and suggested that it is due to differences in internal kinetic energy between cyclic and open-chain compounds. In particular, he predicted that the heat of formation of cyclohexane should be greater than that calculated from the bond-energy sum by an amount equal to the difference between the resonance energy of benzene obtained by the two methods.

Recent data show that in fact the heat of formation of cyclohexane is the same as that calculated from bond energies obtained from the normal paraffins. The discrepancy between the two ways of obtaining resonance

energies of benzene derivatives proves to be due to the use of incorrect bond-energy values. No special explanation in terms of differences in stability between cyclic and open-chain structures is necessary, since the required bond energies may be derived from open-chain compounds.

The bond energies in the normal paraffins reach constant values with increasing chain length. From Rossini's data² for the heats of formation of the paraffins, and values of 126.3 and 51.71 kcal, as the heats of formation per gram atom of carbon and hydrogen, respectively, in their standard states from monatomic gases at 298.1°K3, the the C-C and C-H bond energies are found to be 60.3 and 87.15 kcal. The sum of these bond energies gives the heat of formation of n-hexane exactly, and using them we obtain 1407.6 kcal. for the heat of formation of cyclohexane from atoms, which is in very good agreement with the value of 1407.8 obtained from Rossini's data.4

With the above C-C and C-H values, that for the C=C energy may be obtained from Rossini's data⁵ for the heats of formation of the monoölefin hydrocarbons, which were obtained by combining heats of hydrogenation with specific heat and heat of combustion data. For olefins with the double bond in the 1 position, this tends to a constant value of 101.2 kcal. With these bond energies, the apparent resonance energy of benzene is 41 kcal., in disagreement with hydrogenation result of 36. If, however, the heats of formation of the isomeric olefins are considered, and the other bond energies taken as constant, the C = Cenergy is found to vary from, for example, 101.3 in 1henene to 107.2 in 2,3-dimethyl-2-butene. This is, of course, the well-known substitution effect noted by Kistiakowsky,6 which persists to a considerable extent at 0°K.7 The hexene in which the double bond most nearly resembles that found in an unsubstituted ring is clearly cis 3-hexene, for which the C=C energy is found to be 102.9 kcal. Using this C=C value, we obtain for the resonance energy of benzene 36 kcal. in agreement with the hydrogenation value. Similarly for 0-xylene, two of the C=C bonds may be taken as equivalent to that in 2-methyl-2-butene, and the third as equivalent to that in cis 3-hexene, which reduces the derived resonance energy by 12 kcal. to 34. Again, with Rossini's value for the heat of combustion of styrene,8 and appropriate C=C energies obtained from non-cyclic compounds as before, the resonance energy of styrene obtained by the two methods agrees. That it is legitimate to consider the double bond in a ring structure as similar to a corresponding double bond in an olefin is shown by the fact that the heat of hydrogenation of non-cyclic compounds of the type CHR = CHR' (cis) is the same as that of cyclohexene.

We should point out that while for convenience we have assumed that bond-energy differences are localized in the C=C bond, this is a purely formal treatment; some change may occur in other bond energies.

- Trans, Faraday Soc. 42, 767 (1946). Prosen and Rossini, J. Research Nat. Bur. Stand. 34, 263 (1945).
 Coates and Sutton, to be published.
- Prosen, Johnson, and Rossini, J. Research Nat. Bur. Stand. 37, 51
 - Frosen and Rossini, J. Research Nat. Bur. Stand. 36, 269 (1946).
 Kistiakowsky et al., J. Am. Chem. Soc. 58, 137 (1936).
 Rossini, Chem. Rev. 27, 1 (1940).
 Prosen and Rossini, J. Research Nat. Bur. Stand. 34, 59 (1945).

The Detection of Free Radicals in Hydrogen Atom Reactions

G. M. HARRIS AND A. W. TICKNER Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada July 2, 1947

LARGE number of investigations of reactions of A hydrogen atoms with various substances have been made making use of the discharge tube method of Wood and Bonhoeffer. With organic vapors, the mechanisms of such reactions have invariably been explained in terms of free organic radical chains.2 However, no direct evidence for the existence of free radicals in such reacting mixtures has heretofore been reported. The Paneth-Rice technique for the detection of free radicals,3 successfully applied in the past to photo-chemical and thermal decomposition reactions, has been recently adapted by the present authors to the hydrogen atom reaction problem.

A mirror of metal known to be insensitive to atomic hydrogen but sensitive to free organic radicals was deposited by condensation in a vacuum on a water-cooled glass finger, and introduced into the reaction chamber of the apparatus. Bismuth was adopted as the mirror metal in our work because of the ready availability (from uranium extraction residues) of its radioisotope of atomic weight 210, the activity of which is eminently suitable for tracer use. Preliminary experiments confirmed the non-removal of a radioactive bismuth mirror in the presence of atomic hydrogen alone, thus eliminating the possibility of the formation of a stable volatile hydride under the conditions of our experiments.

A volatile compound known to be easily decomposed at room temperature by atomic hydrogen, dimethyl mercury, was selected for trial. Previous work4 had suggested a free radical mechanism to explain the products, which are free mercury and a methane-ethane mixture. It was readily demonstrated that no direct reaction occurred between the dimethyl mercury vapor and the bismuth mirror in the absence of atomic hydrogen within the temperature range 20° to 45°C. With the mirror maintained at 20°C, which was about 5° cooler than the prevailing room temperature, the presence of the hydrogen atom-dimethyl mercury reaction mixture resulted in a rapid clouding up of the mirror with condensed mercury vapor, and within a few minutes it was completely concealed by mercury droplets. Radioactivity measurements indicated that part of the bismuth was transported to a trap cooled in liquid air, some distance removed from the reactor, and recoverable from this trap as a volatile compound. However, after 20 minutes treatment most of the bismuth still remained on the cooled finger, apparently amalgamated with the mercury.

The experiment was repeated, this time maintaining the bismuth mirror at a temperature of 45°C. In this case, the mirror disappeared almost completely within the 20-minute reaction period, and the resulting volatile bismuth compound was shown to have been transported to the liquid air trap by means of radioactivity measurements, as before. The mercury formed in the reaction condensed as a grayish fog on the surrounding walls of the reactor, which were at