this will lead to a better understanding of solubility in terms of the molecular structure of the polymeric solute and the liquid. The results of such studies will be reported in subsequent publications.

Registry No. (Styrene)·(divinylbenzene) (copolymer), 9003-70-7.

References and Notes

(1) Errede, L. A.; Stoesz, J. D.; Sirvio, L. M. *J. Appl. Polym. Sci.*, in press.

(2) Errede, L. A. *J. Appl. Polym. Sci.*, in press. Presented in part before the Society of Polymer Science, Japan, May 1985 (*Polym. Prepr. Jpn.* **1985**, *34*(1), 9), and in part before the American Chemical Society, Sept 1985 (*Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26*(2), 77).

(3) Errede, L. A.; Newmark, R. A.; Hill, J. R. *Macromolecules* **1986**, *19*, 651. Errede, L. A. *Macromolecules* **1986**, *19*, 654.

(4) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(5) Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Reinhold: New York, 1950.

(6) Gee, G. *Trans. Faraday Soc.* **1946**, *42*, 585.

(7) Hoy, K. L. *Paint Technol.* **1970**, *42*(541), 76. Hoy, K. L. *Tables of Solubility Parameters*, 1975, a bulletin published by Union Carbide Corp.

(8) *A Three Dimensional Approach to Solubility*, a bulletin published by Eastman Co.

(9) Hansen, C. M.; Skaarup, K. J. *Paint Technol. Mol.* **1976**, *39*, 505.

(10) Barton, A. F. F. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Boca Raton, FL, 1983.

(11) Boyer, R. F.; Spencer, R. S. *J. Polym. Sci.* **1948**, *3*, 97.

(12) Magat, M. J. *Chem. Phys.* **1949**, *46*, 344.

(13) Scott, R. L.; Magat, M. *J. Polym. Sci.* **1949**, *4*, 555.

(14) Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers*; Elsevier: New York, 1976; 130.

(15) Scatchard, G. *Chem. Rev.* **1945**, *44*, 7.

(16) Small, P. A. *J. Appl. Chem.* **1949**, *3*, 71.

(17) Gutman, V. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978.

(18) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* **1971**, *93*, 6014.

(19) Drago, R. S.; Parr, L. B.; Chamberlain, C. S. *J. Am. Chem. Soc.* **1977**, *99*, 3203.

(20) Fowkes, F. W.; Tischler, P. O.; Wolfe, J. A.; Lannigan, L. A.; Ademu-John, C. M.; Halliwell, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 547.

Polymer Swelling. 6. A Study of Poly(styrene-*co*-divinylbenzene) Swelling in Liquids of the Homologous Series $Ph(CH_2)_nH$

L. A. Errede

3M Science Research Laboratories of Central Research, 3M Center, Building 201-2N-22, St. Paul, Minnesota 55144. *Received October 17, 1985*

ABSTRACT: It is shown that the relative swelling power, C, for styrene-*co*-divinylbenzene polymers exhibited by liquids in the homologous series $Ph(CH_2)_nH$ decreases monotonically with n from $n = 0$ to $n = 10$; the relationship of C in terms of n for the first five members of the homologous series is given by $C = 2.10 - 0.108n$. Thereafter, C deviates negatively from this line by an amount Δ given approximately by $\Delta = 0.07m$, where $m = n - 6$ for all $n > 5$ and also by $\Delta = 0.04F_{cmo}^2 + 0.06F_{cmo} + 0.02$, where $F_{cmo} = 1.15m^{1/2} - 0.81$ is the force of correlated molecular orientation measured by others for association of liquids in the homologous series $H(CH_2)_nH$. A similar pattern is exhibited in the correlation of C with δ, the Hildebrand solubility parameter; i.e., C is a linear function of $(9.5 - \delta_{liq})^2$ for liquids $Ph(CH_2)_{n<7}H$, but it deviates negatively from the line $C = 2.19 - 0.60(9.5 - \delta_{liq})^2$ by an amount $d = 0.33F_{cmo}$ for liquids $Ph(CH_2)_{n>6}H$.

Introduction

We reported[1-3] that the swellability, S, of styrene-*co*-divinylbenzene polymers at equilibrium with excess liquid is related to the average number of atoms, λ, in the backbone of the polystyrene segments between cross-link junctions by the equation

$$S = C(\lambda^{1/3} - \lambda_0^{1/3}) \qquad (1)$$

where C is the swellability consant of the liquid with respect to Sty-*co*-DVB and λ_0^{-1} is the critical cross-link density of the polymer above which $S = 0$. Correlation of C with the corresponding Hildebrand solubility parameter, δ, of the swelling liquids[4] showed that δ_{Sty} determined thereby depends on the class of liquids used to make such correlations. Thus, $\delta_{Sty} = 9.5$ for substituted benzenes, 9.2 for chlorocarbons, 9.1 for ketones, 8.4 for esters, and 7.3 for ethers. When C was correlated with the corresponding $(\delta_{Sty} - \delta_{liq})^2$ for the lower members of the homologous series $Z(CH_2)_nH$, a set of parallel lines was obtained given approximately by the general equation

$$C = A - 0.60(\delta_{Sty} - \delta_{liq})^2 \qquad (2)$$

where A was 2.19 for Z = Ph, 1.48 for esters, 1.42 for ketones, and 0.64 for ethers.[4]

This implies that the major factor that determines swelling and/or solvent power of a given liquid for Sty-*co*-DVB polymers is the affinity of the functional group Z of that liquid for the polymer components, especially the pendant phenyl group,[4] and that the $(CH_2)_nH$ attached to Z mitigates this affinity in accordance with the additive contribution of each CH_2 group as suggested by Scatchard[5] and Small.[6]

It was of interest, therefore, to see if eq 2, which was observed to be applicable for the lower members of the homologous series $Z(CH_2)_nH$, i.e., for $n < 5$, is also valid for the higher members of these series, i.e., for $n > 5$. To this end I decided to study first the relationship of C as a function of n, from 0 to 10, for liquids in the homologous series $Ph(CH_2)_nH$ and then to correlate C with $(9.5 - \delta)^2$, where δ_n is the solubility parameter of the nth member of the homologous series. The purpose of this publication is to report the results of that study.

General Procedure

The test liquids listed in Table I were obtained from commercial sources, mostly from Aldrich Chemical Co., and were used without further purification. The Sty-*co*-DVB polymers made to undergo swelling in these liquids were obtained from Bio-Rad Laboratories. Aliquots of these polymers in the form of microbeads (the DVB

Table I
Relative Swelling Power, C, of $Ph(CH_2)_nH$ for Poly(Sty-*co*-DVB)

n	C	$\lambda_0^{1/3}$	d	δ_n	$(9.5 - \delta_n)^2$ [c]
0	2.14	1.76	0.878	9.16a	0.12
1	2.00	1.78	0.867	8.93a	0.32
2	1.84	1.77	0.867	8.84a	0.44
3	1.78	1.78	0.862	8.64a	0.74
4	1.69	1.95	0.860	8.58a	0.85
5	1.53	1.95	0.863	8.50b	1.00
6	1.45	2.00	0.861	8.44b	1.12
7	1.30	2.04	0.860	8.39b	1.23
8	1.07	2.05	0.861	8.35b	1.32
9	0.92	1.75	0.858	8.31b	1.42
10	0.74	1.85	0.856	8.28b	1.49

[a] Data reported by Hoy[7] and/or by Hansen.[8] [b] Data calculated by the method of group contributions as outlined by Van Krevelen.[9] [c] 9.5 is the solubility parameter of poly(Sty-*co*-DVB) in $cal^{1/2}/cm^{3/2}$ with respect to liquids in this homologous series and to simple mono- or disubstituted benzenes in general.

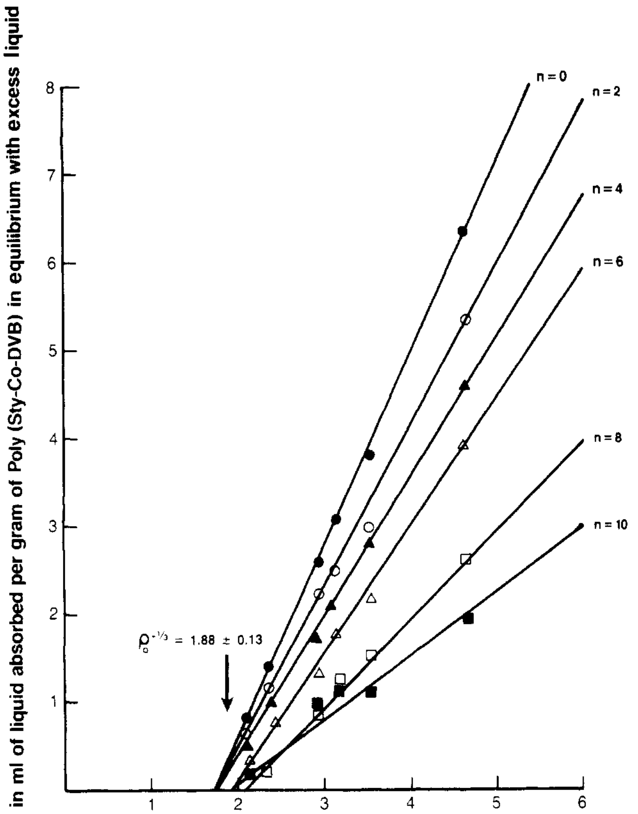


Figure 1. Observed swelling, S (in milliliters of liquid absorbed per gram of poly(Sty-*co*-DVB)), caused by liquids $Ph(CH_2)_nH$ as a function of n and $\lambda^{1/3}$, where $\lambda^{-1/3}$ is the cross-link density of the polymer.

mole fractions of which ranged from 0.01 to 0.12) were converted into thin microporous films of the microbeads enmeshed in PTFE microfibers as described previously.[1] The magnitude of swelling, S (in milliliters of liquid absorbed per gram of Sty-*co*-DVB at equilibrium with excess liquid), was measured in the usual way[1] as a function of the cross-link densities of the same set of six composite films characterized previously.[1] The swelling constants C and $\lambda_0^{1/3}$ observed for these liquids are collected in Table I. Also collected therein are the corresponding solubility parameters, δ, for the liquids in the homologous series $Ph(CH_2)_nH$. Those for the liquids with $n < 5$ were reported by Hoy[7] and Hansen.[8] Those for liquids with $n > 5$ were calculated by the method outlined by Van Krevelen;[9] i.e., δ_{n+1} was calculated from δ_n beginning with the reported $\delta_{n=4} = 8.58\ cal^{1/2}/cm^{3/2}$ and density, 0.860 g/mL, for $Ph(CH_2)_4H$ using the method of additive CH_2 group contributions to total cohesive energy, $E_{coh} = \delta^2 V$, and to molar volume V as outlined in the text.[9]

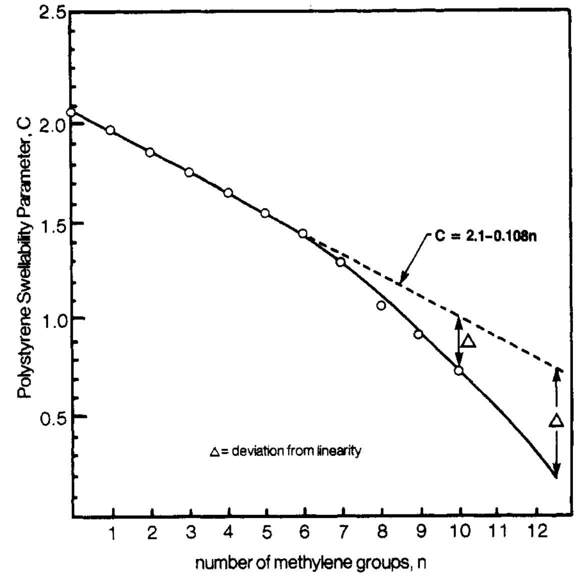


Figure 2. Relative swelling power, C (in milliliters of liquid absorbed per gram of poly(Sty-*co*-DVB)), exhibited by liquids in the homologous series $Ph(CH_2)_nH$ as a function of n.

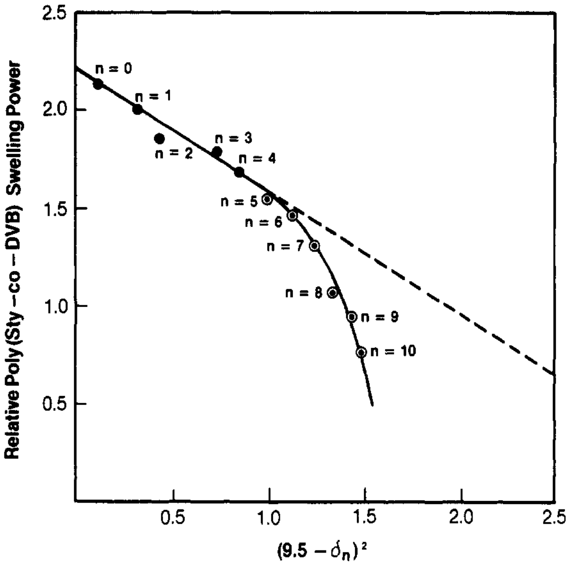


Figure 3. Correlation of relative swelling power, C, for poly(Sty-*co*-DVB) with the corresponding $(9.5 - \delta_n)^2$, where δ_n is the solubility parameter of the liquid $Ph(CH_2)_nH$.

Results and Discussion

The plot of S as a function of $\lambda^{1/3}$ for each of the liquids listed in Table I was a straight line (Figure 1) in accordance with eq 1. The observed $\lambda_0^{1/3}$ for this set of 11 liquids with the general formula $Ph(CH_2)_nH$ was statistically constant at 1.88 ± 0.12 (i.e., $\lambda_0^{-1} = 0.13–0.18$), which is slightly higher than the corresponding average reported for the set of 20 substituted benzenes listed in Table I of ref 4; i.e. $\lambda_0^{1/3} = 1.77 \pm 0.07$ ($\lambda_0^{-1} = 0.16–0.20$). In contrast to this constancy the observed relative swelling power, C, determined from the slope of these lines (Figure 1) decreased monotonically with n from $C = 2.14$ for $n = 0$ to 0.74 for $n = 10$ (Table I and Figure 2).

Since the solubility parameters for members of the homologous series $Ph(CH_2)_nH$ with $n > 4$ have not been reported, these were calculated by the method outlined by Van Krevelen as indicated above. Subsequent correlation of C for $n = 0$ to $n = 10$ with the corresponding $(9.5 - \delta_n)^2$ (Figure 3) shows that the linear relationship established earlier[4] with the limited data for $n < 5$ is in fact valid only for $n < 7$. Thereafter, C deviated negatively from the line

$$C = 2.19 - 0.60(9.5 - \delta_n)^2 \qquad (3)$$

by an amount d, given approximately by $d = 0.4m^{1/2}$, where $m = n - 6$ for $n > 5$.

In contrast, the corresponding correlation of C for simple mono- and disubstituted benzenes (Figure 2 of ref 4) shows no deviation from linearity over a greater range of $(9.5 - \delta_{\text{liq}})^2$, which rules out the possibility that deviation always occurs whenever $(9.5 - \delta_{\text{liq}})^2$ becomes relatively large. It was concluded, therefore, that the deviation exhibited by the homologous series $Ph(CH_2)_nH$ (Figure 2 and 3) is caused by the poly(methylene) group, presumably owing to molecular association when $n > 6$.

This conclusion is consistent with the observation made by Botherel et al.[10,11] as a result of their study of light scattering by liquids in the homologous series $H(CH_2)_nH$, namely that light scattering is observed when $n > 6$ and that the magnitude increases as a function of $m = n - 6$ for all values of $n > 5$. They attributed this to molecular association owing to alignment of parallel $-(CH_2)-$ chains when $n > 6$. The same conclusion was arrived at by Tancrede et al.[12] on the basis of their calorimetric studies of the heats of mixing of the higher members of this homologous series ($n > 6$) with the lower members ($n < 6$) and also by Fowkes[13] on the basis of his surface tension studies. This additional force of association was named[13] the force of "correlated molecular orientation", F_{cmo}, and was observed to increase with $m = n - 6$ for $n > 5$ as follows: $n = 6$, $F_{\text{cmo}} = 0$; $n = 7$, $F_{\text{cmo}} = 0.38$; $n = 8$, $F_{\text{cmo}} = 0.87$; $n = 9$, $F_{\text{cmo}} = 1.16$; $n = 10$, $F_{\text{cmo}} = 1.46$; $n = 11$, $F_{\text{cmo}} = 1.70$; $n = 12$, $F_{\text{cmo}} = 2.04$; $n = 14$, $F_{\text{cmo}} = 2.47$; $n = 16$, $F_{\text{cmo}} = 2.89$. This relationship of F_{cmo} (in dyn/cm) as a function of $m = n - 6$ for $n > 5$ in the homologous series $H(CH_2)_nH$ can be expressed by

$$F_{\text{cmo}} = 1.15m^{1/2} - 0.81 \qquad (4)$$

This relationship is in good register with respect to n with both the deviation from linearity Δ observed in Figure 2 and the deviation from linearity d observed in Figure 3. It was determined empirically that F_{cmo} is related to the former by the equation

$$F_{\text{cmo}} = 4.84\Delta^{1/2} - 0.67$$

and to the latter by the equation

$$F_{\text{cmo}} = 3d$$

The magnitudes of both Δ and d, therefore, appear to be measures of the degree to which self-association of the liquid, owing to F_{cmo} for all liquids in the homologous series $H(CH_2)_{n>6}Ph$, causes additional steric hindrance to association of the Ph group of the liquid with the pendant Ph group of poly(Sty-*co*-DVB). For the purpose of interpreting swellability in terms of the molecular structures of the polymer and the swelling liquid, Figure 2 is more useful than Figure 3 as a base line for comparisons that show how alteration of the molecular side chain affects the swelling power of liquids $Ph(CH_2)_nH$ or their derivatives. Thus, comparison of xylenes (Table I of ref 4) with ethylbenzene shows that the relative swelling power of these liquids is in the order *o*-xylene ($C = 2.02$) > EtPh ($C = 1.84$) > *m*-xylene ($C = 1.80$) > *p*-xylene ($C = 1.73$). The effect of molecular alteration of the side chain is even more marked when the alteration produces a six-membered ring; thus phenylcyclohexane ($C = 1.80$) > 1-phenyl-*n*-hexane ($C = 1.45$), and tetrahydronaphthalene ($C = 2.22$) > 1-phenyl-*n*-butane ($C = 1.69$). Branching in the aliphatic side chain ($n < 6$) sometimes causes a small decrease in swelling power, i.e., *n*-propylbenzene ($C = 1.78$) > isopropylbenzene ($C = 1.65$), but not in the case of *tert*-butylbenzene ($C = 1.69$), which is the same as *n*-butylbenzene ($C = 1.69$).

Similarly, the swelling power of cyclic aliphatic hydrocarbons with respect to poly(Sty-*co*-DVB) is greater than the corresponding linear aliphatic hydrocarbons. Thus, cyclohexane ($C = 0.53$) > *n*-hexane ($C = 0$), and *cis*-decahydronaphthalene ($C = 1.00$) > *trans*-decahydronaphthalene ($C = 0.41$) > *n*-decane ($C = 0$).

When substituents such as Cl, Br, I, NO_2, and CH_3 are attached directly to the aromatic ring, they affect the swelling power of that liquid (Table I of ref 4) about as expected on the basis of (a) the electronic contribution to the π-electrons of the phenyl ring, which affects accordingly its affinity for the phenyl group of the polymer, and (b) the mass contribution to the size of the aromatic grouping, which affects sterically its ability to accommodate the phenyl group of the polymer. When these groups are not attached directly to the π-electron system, however, the effect appears to be an additive combination of their respective individual affinities for the phenyl group of the poly(Sty-*co*-DVB). Thus, $PhCH_2Cl$ ($C = 2.39$) > $PhCH_3$ ($C = 2.00$), and $PhCH_2O_2CCH_3$ ($C = 1.94$) > $PhCH_2OEt$ ($C = 1.85$) > $Ph(CH_2)_3H$ ($C = 1.78$).

Summary and Conclusions

It was shown that the linear correlation of C with $(9.5 - \delta_n)^2$ (Figure 2) for the homologous series of liquids $Ph(CH_2)_nH$ is valid only for $n = 0$–6. Thereafter C deviates negatively from the line $C = 2.19 - 0.60(9.5 - \delta_n)^2$ by an amount $d = 0.33F_{\text{cmo}}$, where F_{cmo} is the force of correlated molecular orientation determined by others[10-13] for liquids in the homologous series $H(CH_2)_{n>6}H$. The magnitude of this force increases with $m = n - 6$ for all $n > 5$ as given by $F_{\text{cmo}} = 1.15m^{1/2} - 0.81$. Similarly, C for liquids in the homologous series $Ph(CH_2)_nH$ is a linear function of n for $n = 0$–5 (Figure 2), and thereafter C deviates negatively from the line $C = 2.1 - 0.108n$ by an amount Δ given approximately by $\Delta = 0.07m$ and by

$$\Delta = 0.04F_{\text{cmo}}^{\ 2} + 0.06F + 0.02$$

The usual method for calculating Hildebrand solubility parameters for aromatic hydrocarbons by molecular group contributions[9] considers only the contribution to cohesive energy and molar volume. Consequently such operations in the calculation of δ for $Z(CH_2)_{n>6}H$ will lead to erroneous results, owing to F_{cmo}, which increases with $m = n - 6$.

With the observed relationship of C as a function of n (Figure 2) as a base line for comparison, it was noted that branching in the aliphatic side chain for $n < 5$ does not cause a significant effect on swelling power unless the molecular modification results in ring formation, such as in cyclohexylbenzene or in tetrahydronaphthalene, in which case C is increased significantly. This is consistent with earlier comparisons of relative swelling power for poly(Sty-*co*-DVB), i.e., cyclohexane ($C = 0.53$) > *n*-hexane ($C = 0$), and *cis*-decahydronaphthalene ($C = 1.00$) > *trans*-decahydronaphthalene ($C = 0.41$) > *n*-decane ($C = 0$).

Registry No. (Styrene)·(divinylbenzene) (copolymer), 9003-70-7.

References and Notes

(1) Erréde, L. A. *J. App. Polym. Sci.*, in press. Presented in part before the Society of Polymer Science, Japan, May 1985 (*Polym. Prepr. Jpn.* **1985**, *34*(1), 9) and in part before the American Chemical Society, Sept 1985 (*Polym. Prepr.* (*Am. Chem.*

Soc., Div. Polym. Chem.) **1985**, *26*(2), 77).
(2) Errede, L. A.; Newmark, R. A.; Hill, J. R. *Macromolecules* **1986**, *19*, 651.
(3) Errede, L. A. *Macromolecules* **1986**, *19*, 654.
(4) Errede, L. A. *Macromolecules*, preceding paper in this issue.
(5) Scatchard, G. *Chem. Rev.* **1945**, *44*, 7.
(6) Small, P. A. *J. Appl. Chem.* **1949**, *3*, 71.
(7) Hoy, K. L. *Paint Technol.* **1970**, *42*(541), 76. Hoy, K. L. *Tables of Solubility Parameters*, 1975, a bulletin published by Union Carbide Corp.
(8) Hansen, C. M.; Skaarup, K. J. *Paint Technol.* **1967**, *39*, 505.
(9) Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers*; Elsevier: New York, 1976; Chapter 7.
(10) Botherel, P. *J. Colloid Sci.* **1968**, *27*, 529.
(11) Tancrede, P.; Patterson, D.; Botherel, P. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 29.
(12) Tancrede, P.; Botherel, P.; de St. Romain, P.; Patterson, D. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 15.
(13) Fowkes, F. W. *J. Phys. Chem.* **1980**, *84*, 510.
(14) Hildebrand, J. C.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Reinhold: New York, 1950.
(15) Keller, R. A.; Karger, B. L.; Snyder, L. R. In *Gas Chromatography*; Stock, R., Perry, S. G., Eds.; Institute of Petroleum; London, 1971; p 125.
(16) Barton, A. F. N. *Handbook of Solubility Parameters and Other Cohesion Parameters*; CRC: Boca Raton, FL, 1983.

Electropolymerization of Cyanogen in the Presence of a Heterocyclic Anion

J. H. Chen and M. M. Labes*

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122.

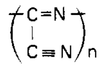
Received November 13, 1985

ABSTRACT: Cyanogen is electropolymerized by using salts of the heterocyclic anion $C_7N_7^-$ as the electrolyte in order to understand the nature of the polymerization process in more detail. Even though such preparations give low molecular weights between 400 and 900, the polymer still has fiber-forming properties and can be converted to carbon fibers. It is estimated from ^1H NMR and calorimetric measurements that one heterocyclic anion per 40 cyanogen monomers is incorporated as either a chain end or within the chain and that the alkylammonium cation serves as a closely bound gegenion.

Introduction

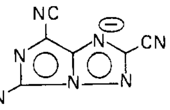
We have recently reported the preparation of poly(cyanogen) (PCN) (I) via the electropolymerization of cyanogen (ethanedinitrile, C_2N_2) in acetonitrile containing an electrolyte such as tetraethylammonium tetrafluoroborate.[1,2] Spectroscopic data indicated that the reaction proceeds via the initial formation of a heterocyclic anion, $C_7N_7^-$ (II) (1*H*-imidazo[1,5-*b*]-*s*-triazole-2,5,7-tricarbonitrile), from the reaction of C_2N_2 with CN^- produced at the cathode by a one-electron reduction. A small amount of $C_7N_7^-$ or dimeric forms derived therefrom could possibly be incorporated in the polymer, but no assessment of the amount could be made via NMR, infrared, or UV-visible spectroscopy. The spectral characteristics of the black polymers have been presented earlier.[1]

I



$$\left(\overset{\displaystyle -C=N-}{\underset{\displaystyle C\equiv N}{|}}\right)_n$$

II



In order to further understand this problem, it was decided to utilize $Et_4N^+C_7N_7^-$ as the electrolyte to maximize the likelihood that incorporation of derived structures occurs. ^1H NMR allows the assessment of the tetraethylammonium moieties in the polymer, whereas differential scanning calorimetric studies (DSC) indicate an exothermic peak always occurs when the heterocyclic anion is heated to about 630–640 K. By employing these methods, it is possible to determine the extent of incorporation of $C_7N_7^-$ into PCN.

PCN prepared in this way was found to have lower molecular weight than that prepared with conventional electrolytes. In spite of the molecular weight being only 400–900, the polymer still has film- and fiber-forming properties and can be converted to carbon fibers.

Experimental Procedures

The preparation of $Et_4NC_7N_7$, $Me_4C_7N_7$, and HC_7N_7 followed the procedure of Wiley et al.[3] Acetonitrile (U.V. grade, Burdick & Jackson Laboratories) was distilled over CaH_2 in an inert atmosphere and stored under high-purity nitrogen. Cyanogen gas (minimum purity 99%) from Matheson Gas Products contained, by analysis, 5 ppm O_2, 23 ppm N_2, and 50 ppm H_2O. It was purified by passing it through a scrubbing train that consisted of a silver nitrate bubbler (to remove hydrogen cyanide), a calcium chloride tower, a sodium hydroxide tower (to remove carbon dioxide), and a phosphorus pentoxide tower to remove traces of water. A typical polymerization was performed as follows. Polymerizations were initiated electrochemically in cells that consisted of two circular glassy carbon electrodes 2.5 cm in diameter and 1 cm apart. The total volume of the cell was about 100 mL. The experiments were conducted under conditions of constant voltage with a dc power supply (Hewlett-Packard 611A). Typically, the voltage was held between 5 and 15 V (at an initial current of 50–80 mA) for 72 h. Cyanogen was bubbled through dry acetonitrile containing about 0.02 M electrolyte. The cyanogen concentration was determined to be 1.2 M by potentiometric titration. For this determination, a 1-mL aliquot was added to 30 mL of 0.1 M KOH solution, cyanogen was disproportionated into CN^- and CNO^-, and a titration was performed with a stock silver nitrate solution employing a silver electrode (Orion Model 701A digital pH/mv meter) to detect the end point.

Polymer formed both at the anode and in solution. In the early stages of polymerization, the polymer formed a coherent thin film on the carbon electrode, which started to flake and peel off as the reaction proceeded further. The solution polymeric product was precipitated by pouring the solution into a 1:2 mixture of CH_3CN and ethyl ether, kept dry inside a glovebox, giving a black solid. The unreacted electrolyte dissolves in the CH_3CN/ether (1:2) mixture. The yield of the polymer is typically approximately 75% based on the $(CN)_2$ used. The crude polymeric products were submitted for elemental analysis and molecular weight

0024-9297/86/2219-1528$01.50/0