Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymerization of β-Ethynylnaphthalene

Richard H. Wiley[a]; Joseph Y. Lee[b]
[a] City University of New York, New York, New York [b] RAI Research Corp., Hauppage, Long Island, New York

To cite this Article Wiley, Richard H. and Lee, Joseph Y.(1971) 'Polymerization of β-Ethynylnaphthalene', Journal of Macromolecular Science, Part A, 5: 3, 507 — 511

To link to this Article: DOI: 10.1080/00222337108061039

URL: http://dx.doi.org/10.1080/00222337108061039

J. MACROMOL. SCI.–CHEM., A5(3), pp. 507-511, May, 1971

Polymerization of β-Ethynylnaphthalene

RICHARD H. WILEY
City University of New York
New York, New York 10021

and

JOSEPH Y. LEE
RAI Research Corp.
Hauppage, Long Island, New York

SUMMARY

Poly (β-ethynylnaphthalene), which has not been previously prepared and characterized in detail, was prepared with a Ziegler-Natta type catalyst. The polymer is reddish in color, soluble in aromatic solvents, and gives a positive color test for conjugation with antimony trichloride. The polymer has a molecular weight of up to 2091. Its IR and UV spectroscopic characteristics are in accord with a modified conjugated polyene structure. It is thermally stable up to 470°, and probably partially crystalline.

The only previously recorded report on the polymerization of ethynylnaphthalene is that of α-ethynylnaphthalene by aluminum triethyl and transition metal chelates [1]. It does not provide data about the polymer needed for other purposes [2] of current interest. We have, therefore, undertaken a study of the polymerization of β-ethynylnaphthalene and report our results herein.

EXPERIMENTAL

The monomer, β-ethynylnaphthalene, was prepared from 2-acetonaphthone according to Robin's procedure [3], modified in the dehydrohalogenation step by using potassium hydroxide in absolute ethanol instead of potassium ethoxide. The monomer was polymerized with varying proportions of triisobutyl aluminum and titanium tetrachloride as the catalyst. Both polymerization and recovery were done under nitrogen atmosphere. This consists of washing the polymer with hydrochloric acid in methanol solution to remove the metal catalyst, dissolving the reaction mixture in benzene, and precipitating the polymer with excess methanol. The polymer was then dried in vacuo overnight. IR spectra were taken in potassium bromide pellets with a Perkin-Elmer IR 21. Electronic spectra were taken in carbon tetrachloride with a Cary 14 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were obtained with a Varian V4502-15 spectrometer equipped with a Fieldial magnetic field regulator operating in a high-power mode. Spin concentrations were calculated by comparing with a calibrated standard of pitch in potassium chloride supplied by Varian. Differential thermal analysis was performed by a Dupont 900 Thermal Analyser. The number-average molecular weight was measured with a vapor pressure osmometer by Schwarzkopf Microanalytical Laboratory.

RESULTS AND DISCUSSION

As presented in Table 1, the yield of the polymer depends on the molar ratio of triisobutyl aluminum to titanium tetrachloride. The maximum yield occurs at a ratio of Al:Ti = 2.8. Data on the optimum ratio of Al:Ti in ethynylnaphthalene polymerization is not available, but data on acetylene polymerization is reported to be 2-2.5 [4]. The molecular weight of the polymer is greatest at this catalyst ratio also. The highest molecular weight, 2091, corresponding to a degree of polymerization 14, was obtained at a catalyst ratio in which the yield of the polymer was also a maximum. No molecular weight data on ethynylnaphthalene polymers is known to date, but the molecular weights of acetylenic polymers are known to be in the 10^3 range. In the molecular weight ranges encountered, a small amount of solvent or impurities in the polymer will greatly depress the number-average molecular weight. The color of the polymer is between light brown and red, and the melting range by the capillary method is 190-230° (uncorrected).

Table 1. Polymerization of β-Ethynylnaphthalene with Aluminum Tri-isobutyl and Titanium Tetrachloride Catalyst

Monomer (mole/l)	$TiCl_4$ (mole/l)	Al (i-Bu)$_3$ (mole/l)	Molar ratio Al:Ti	Polymerization yield (%)	$\bar{M}_n$	M_p capillary (°C)
0.125	2.4×10^{-2}	6.1×10^{-2}	2.8	44.1	2091	190-200
0.125	2.4×10^{-2}	2.1×10^{-2}	0.9	4.9	495	220-230
0.125	2.4×10^{-2}	10.1×10^{-2}	4.9	31.0	1050	220-210

Characterization

The polymer gives a green color test with antimony trichloride in chloroform which has been used to test the presence of a conjugated double bond system [5, 6]. The IR spectra show that the 3300 and 2100 cm^{-1} bands in the monomer which are assigned to the C–H and –C≡C– stretching frequencies disappear in the polymer, establishing that polymerization has taken place. The band at 1600 cm^{-1}, assigned to fully conjugated double bonds [7, 8] increases in intensity in the polymer. A new band at 2930 cm^{-1}, absent in the monomer, appears in the polymer spectrum, indicative of the presence of an aliphatic group. The 2930 cm^{-1} band is consistent with the mechanism of the Ziegler-Natta type polymerization which requires one end group of the polymer be derived from the alkyl group of the organometallic catalyst [9]. The other bands are common to both the monomer and the polymer. Thus, the naphthyl groups absorb at 885 (1 isolated hydrogen), 850, 810 (2 adjacent hydrogens), and 745 cm^{-1} (4 adjacent hydrogens).

The electronic spectrum of the polymer is entirely different from that of the monomer. There are three major peaks in the monomer at 277, 286, and 298 mμ, and three minor peaks at 315, 325, and 336 mμ. These peaks all disappear in the polymer which exhibits no discrete absorption maxima, but rather a continuous absorption from the UV into the visible region. The absorption is stronger at short wavelengths than at long wavelengths. Such a spectrum has been attributed to a polymer structure that has a conjugated double bond system with increasing number of conjugated double bonds [10].

The polymer, but not the monomer, is paramagnetic and gives an EPR signal. The EPR spectrum of the polymer is a singlet with no resolved hyperfine structures. The same behavior has been observed for polyacetylene and polyphenylacetylene. The EPR curve is of Gaussian shape with a line width of 12 G. The g value of the polymer is very close to that of a free electron. The number of paramagnetic particles in the polymer is estimated to be 10^{16} spins/g. The paramagnetism of the polymer is consistent with a structure with a conjugated double bond stabilized free radicals.

The thermal properties of the polymer were evaluated by differential thermal analysis. The polymer has a melting point of 255° as evidenced by the endotherm. The melting range lies from 200 to 260° as measured by the shift of baseline. The polymer is quite stable up to 470°. At this temperature decomposition sets in as is evidenced by the appearance of an exotherm and enhanced noise in the thermogram. The sharp endotherm indicates that the polymer is at least partially crystalline.

REFERENCES

[1] S. Kambara, M. Hatano, S. Sera, and K. Shimamura, *J. Polym. Sci., Part B*, **5**, 233 (1967).

[2] R. H. Wiley, A. M. Sapse, and J. Y. Lee, *J. Macromol. Sci.–Chem.*, **A4**, 203 (1970).

[3] J. Robin, *Ann. Chim.*, **1931**, 428.

[4] W. H. Watson, Jr., W. D. McMordie, Jr., and L. G. Lands, *J. Polym. Sci.*, **55**, 137 (1961).

[5] A. A. Berlin, *J. Polym. Sci.*, **55**, 621 (1961).

[6] P. A. Plack, *Biochem. J.*, **1961**, 556.

[7] L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.*, **26**, 5163 (1961).

[8] P. M. Duncan and W. G. Forbes, *Polym. Preprints*, **7**, 1035 (1966).

[9] G. Natta, *SPE J.*, **15**, 373 (1959).

[10] P. E. Blatz, *J. Polym. Sci., Part C*, **4**, 1335 (1965).

Accepted by editor September 17, 1970
Received for publication October 12, 1970