Table I
Virial Coefficients and Expansion Factors as a Function of Temperature

t, °C	$A_2 \times 10^5$, $(g^2\ cm^3)/mol$	α^2
34	−9.8	0.341
34.5	−4.1	0.675
35	−2.73	0.908
35.4	0	1.0
36.4	0.29	1.36
45	1.64	2.39
55	3.38	2.82

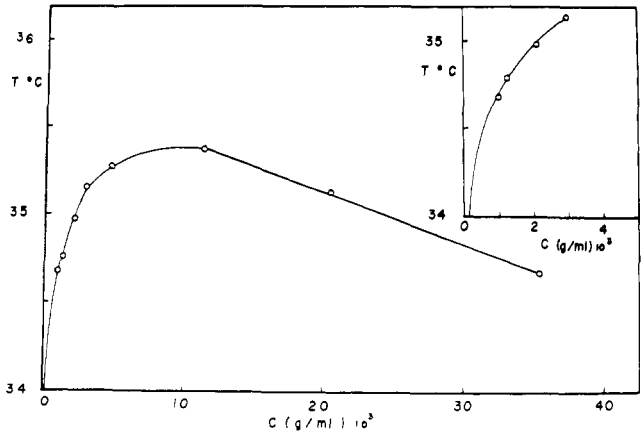

Figure 2. Radius of gyration.

be accurate within approximately 2%.

The phase diagram for this sample was measured and is shown in Figure 1. The critical temperature of this sample was taken to be the maximum in the phase diagram and is 35.4 ± 0.05 °C at a concentration near 1 g/dl. Therefore, the critical temperature is at the theta temperature determined by light scattering. Thus there are no deviations at high molecular weight from the concept of the theta temperature being simultaneously the critical miscibility temperature of an infinite molecular weight sample and the temperature at which the second virial coefficient is zero (see Table I). The critical temperature is in excellent agreement with the linear relation T_c^{-1} vs. $M^{-1/2}$ esablished from lower molecular weight samples[5] and is therefore convincing experimental proof of Casassa's recent comments concerning limiting critical behavior.[6] The light scattering measurements were made at concentrations two to almost three orders of magnitude below the critical concentration, i.e., at 0.02 to 0.002 g/dl. Therefore the solutions used in the light-scattering measurements should phase separate only below 34 °C. Visual observation and photometric scanning confirm the fact that these dilute solutions were not phase separated at 34 °C, the lowest temperature used for the light-scattering measurements.

The z-average radius of gyration of the theta temperature is 2070 Å and Table I lists the values of α^2 the chain expansion factor, where $\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_\Theta$, as well as the virial coefficient. Figure 2 illustrates the dramatic change of the radius as the temperature is lowered from slightly above to slightly below the theta temperature. Even though the temperature changes uniformly in half-degree increments from 35.5 to 34.0 °C, α decreases by an increasing factor. Of course, the lowest value of α is 0.58 which is an order of magnitude larger than the collapse into a sphere containing densely packed segments. Since the virial coefficient is becoming negative at an accelerating rate at this low α, it is unlikely that the single collapsed coil can exist before phase separation begins. However, these data indicate that a polymer coil can be brought to about half its unperturbed size before there is separation into two phases. Further experiments are in progress to determine the nature of high molecular weight polymer coils in this contracted state.

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Chemical Modification of Polymers. 9. Attack of Nitrogen Anions on Poly(vinylbenzyl chloride)

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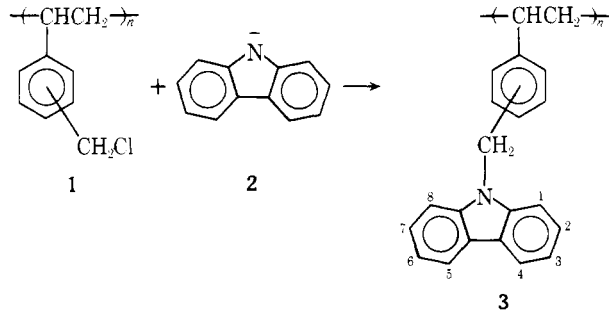
In recent years the chemical modification of polymers has received increasing attention,[1-4] much of it based on Merrifield's use of insoluble resins for synthesis.[5] The ability to continuously vary physicochemical properties of macromolecules by chemical modification has prompted us to examine several such types of reactions on soluble polymers.[6-13] In previous publications we have discussed reactions of poly(vinylbenzyl chloride) (1) with oxygen anions (phenolates) to give polymeric ethers[7] and with Reissert compound carbanions, leading to heterocyclic polymers.[8,9,11-13] In this context the reaction of 1 with nitrogen anions was of interest.

Discussion

(A) Reaction of Potassium Carbazole and Poly(vinylbenzyl chloride). The potassium salt (2) of carbazole was prepared by azeotropic removal of water from an equimolar solution of potassium hydroxide and carbazole in xylene.[14] The solvent xylene was removed and replaced by dimethylformamide (DMF) and a solution of poly(vinylbenzyl chloride)[11] (1) in DMF was added. After stirring 2.5 h, the reaction solution was added dropwise to methanol to yield 97% of the desired poly[(*N*-carbazyl)methylstyrene] (3). Three precipitations from tetrahydrofuran (THF) into ethanol gave a nearly colorless solid, T_g = 152 °C. Anal. Calcd for $C_{15}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.18; H, 5.96; N, 4.84. Gel permeation chromatography (GPC) shows no evidence of any cross-linking or degradation processes in the reaction.



1 2 3

The ultraviolet spectrum of 3 is essentially identical with that of *N*-ethylcarbazole (Figure 1). The infrared spectrum of polymer 3 is quite similar to that of poly(*N*-vinylcarbazole) (Figure 2).

The nuclear magnetic resonance (NMR) spectrum possesses a high field signal (δ 0.5–2) due to the protons of the backbone $CHCH_2$ groupings and a signal at δ ~4.8 due to the

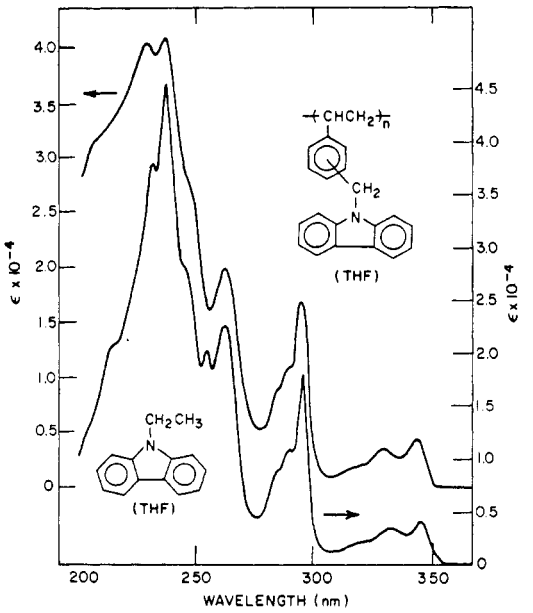


Figure 1. Ultraviolet spectra of THF solutions of poly[(*N*-carbazyl)-methylstyrene] (**3**) (top) and *N*-ethylcarbazole (bottom).

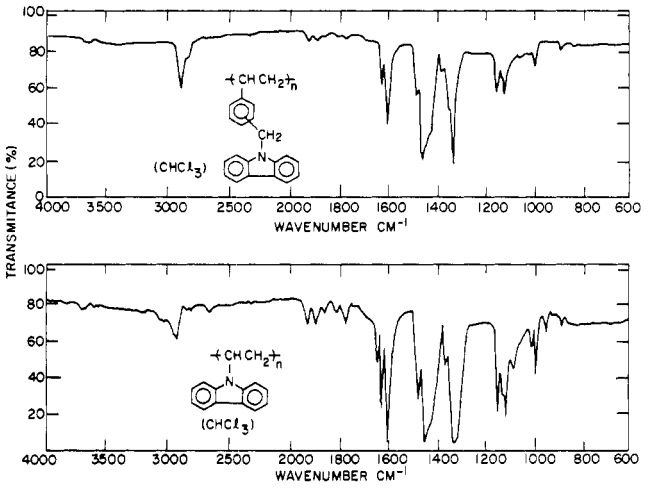
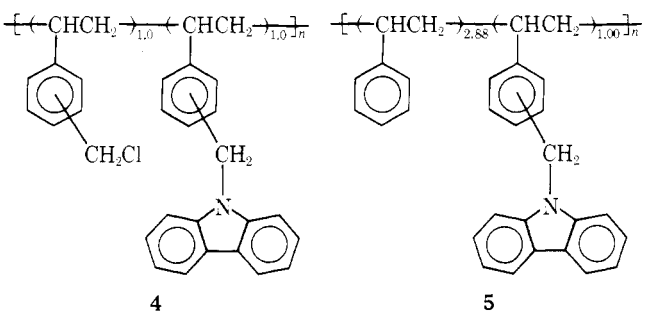


Figure 2. Infrared spectra of $CHCl_3$ solutions of poly[(*N*-carbazyl)-methylstyrene] (**3**) (top) and poly(*N*-vinylcarbazole) (bottom).

benzylic protons and aromatic proton signals. The lowest field signal ($\delta \sim 7.9$) is probably due to protons at the 4 and 5 positions of the carbazole ring. The aromatic proton signals in the region δ 5.4–6.6 are worthy of comment. Polymer **1** has aromatic proton signals at δ 6.4 and 7.0 and these would not be expected to be effected significantly by inductive effects through bonds; thus the signals from δ 6.4 to 5.4 are probably due to protons on the carbazole nucleus. These shielded aromatic protons resemble those seen in poly(*N*- and 2-vinylcarbazoles) (δ 4.8 and 5.8, respectively).[15] The shielding is believed to be due to the interaction of the pendant aromatic groups along the polymer backbone.

The reaction of poly(vinylbenzyl chloride) with half an equivalent of potassium carbazole in the same manner was also found to be quantitative and led to the 1:1 copolymer **4**. Anal. Calcd for $C_{30}H_{26}NCl$: C, 82.64; H, 6.01; N, 3.21; Cl, 8.13. Found: C, 82.49; H, 6.30; N, 3.16; Cl, 8.12. Thus, the composition of the product is readily controlled by stoichiometry in this essentially quantitative reaction, making sequential reactions possible and practical.

Reaction of potassium carbazole with a 2.88:1.00 copolymer[13] of styrene:vinylbenzyl chloride was carried out in analogous fashion. The anticipated copolymer **5**, T_g = 124 °C



(Anal. Calcd for $C_{45}H_{41}N$: C, 90.71; H, 6.94; N, 2.35. Found: C, 89.69; H, 6.84; N, 2.38; Cl, 0.44) was formed in 99% conversion.

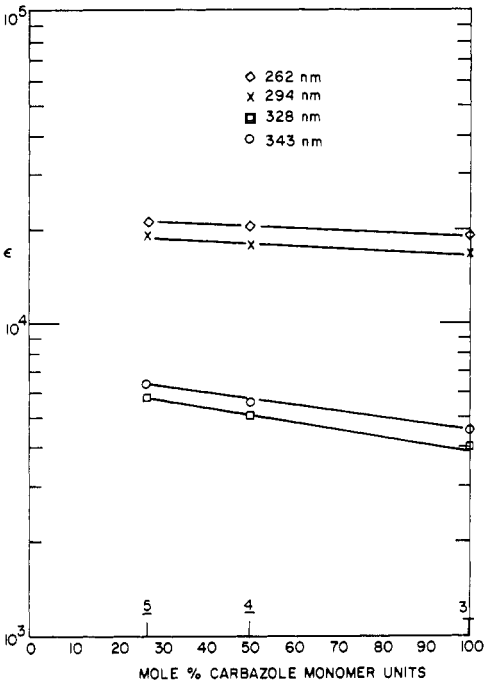
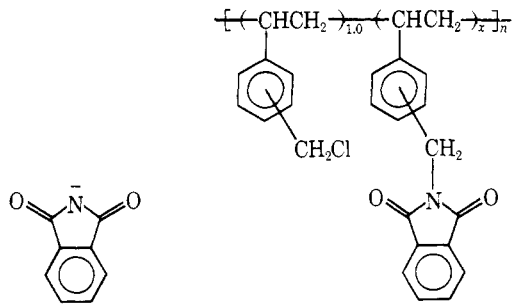


Figure 3. Logarithm of extinction coefficient (ϵ) for 343, 328, 294, and 262 nm peaks vs. mole percent carbazole in polymers **3**, **4**, and **5**.

An interesting fact emerges from the ultraviolet absorption data for **3**, **4**, and **5**. In Figure 3 the exponential dependence of ϵ (calculated on the basis of the carbazole chromophore) on the molar carbazole content of the polymers is shown. Each polymer by itself obeys Beer's law. The result is reminiscent of work on styrene polymers.[16] As previous workers proposed, some sort of interaction between adjacent chromophores, either styrene–carbazole or carbazole–carbazole, is apparently involved as the NMR spectral data above may reflect. Thus as demonstrated in other cases, uv spectroscopy is not dependable for estimation of composition of such polymers.

(B) Reaction of Potassium Phthalimide and Poly(vinylbenzyl chloride). Preparation of the anion **6** by azeotropic removal of water from a xylene solution of phthalimide and KOH, followed by solvent removal and subsequent reaction with polymer **1** in DMF as before, resulted in 64% conversion, i.e., copolymer **7**. Anal. Calcd for $C_9H_9Cl \cdot 1.8C_{17}H_{13}NO_2$: C, 75.91; H, 5.21; N, 4.02; Cl, 5.66. Found: C, 75.05; H, 5.13; N, 3.78; Cl, 5.46. The infrared spectrum of **7** has carbonyl peaks at 1720 and 1770 cm^{-1}. Use of potassium carbonate as the base in DMF in a one-step reaction with **1** at room temperature resulted in 85% conversion; copolymer **8** was isolated. Anal. Calcd for $C_9H_9Cl \cdot 5.7C_{18}H_{13}NO_2$: C, 77.84;



6

7, X = 1.8
8, X = 5.7

H, 4.87; N, 4.63; Cl, 2.07. Found: C, 77.96; H, 5.52; N, 4.53; Cl, 2.23.

Conclusions

An efficient synthesis of poly[(*N*-carbazyl)methylstyrene] (3) by reaction of potassium carbazole (2) and poly(vinylbenzyl chloride) (1) has been developed. Copolymers can be prepared by stoichiometric control of the extent of reaction or through use of copolymers of vinylbenzyl chloride as starting materials for the reaction. The reaction of potassium phthalimide with poly(vinylbenzyl chloride) leads to displacement of 85% of the available chloride ions. Extension ofsye reactions to other N anions such as those from pyrrole and indole seems feasible.

Acknowledgment. The authors thank Dr. G. Sitaramaiah for GPC analyses of polymers, Dr. J. Pochan for T_g measurements, and Dr. W. H. H. Gunther for his continued encouragement.

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CORRECTIONS

"Thermally Induced Phase Separation Behavior of Compatible Polymer Mixtures", by T. Nishi, T. T. Wang, and T. K. Kwei, Volume 8, Number 2, March–April 1975, page 229.

The first lines in the columns on this page should be transposed.

"Conformation of *cyclo*-(L-Leu-L-Tyr-δ-Avaler-δ-Avaler), a Synthetic Inhibitor of Chymotrypsin, by X-Ray Analysis", by I. L. Karle, Volume 9, Number 1, January–February 1976, page 66.

In Figure 5 it would have been more appropriate to compare the experimental ϕ, ψ values for $i > 2$ to fully allowed and partially allowed conformational regions in a map computed for glycyl residues rather than a dipeptide with C^β present. (See Figure 14 rather than Figure 12A in ref 14 which should read pp 328 and 332.) In that comparison, residues with i = 3 and 6 lie within the allowed regions.

"Viscoelastic Properties of Polymer Solutions in High-Viscosity Solvents and Limiting High-Frequency Behavior. II. Branched Polystyrenes with Star and Comb Structures", by J. W. M. Noordermeer, O. Kramer, F. H. M. Nestler, J. L. Schrag, and J. D. Ferry, Volume 8, Number 4, July–August 1975, page 539.

In the legend of Figure 4, the concentration should be 3.25×10^{-2} g/ml; the temperatures should be 9.4, 14.7, 20.0, 25.0, 30.1, and 35.7 °C.