accurate estimate for k_{obsd}, namely $(2.0–2.5) \times 10^{-3}\ s^{-1}$, and confirm the previously reported value of K_2.

We may add that an attempt was made to account for the observed kinetics by invoking the reaction

$$BaBS + S^- \rightleftarrows (BaBS_2)^-$$

but the analysis of such a scheme led to unacceptable results and hence to rejection of the contemplated mechanism.

Comparison of the Dissociations $BaB_2 \rightleftarrows (BaB)^+ + B^-$ and $BaSB \rightleftarrows (BaS)^+ + B^-$.

The former dissociation constant was found to be $K_{BaB_2} = 1.65 \times 10^{-5}$ M whereas the latter is claimed to be $K_b = 3.6 \times 10^{-5}$ M. The statistical factor of 2 appearing in K_{BaB_2} but not in K_b magnifies this difference even more. It seems that the tight association of S^- ion with Ba^{2+} reduces the attraction of B^- in BaSB, while BaB_2 aggregate probably should be considered as a loose one.

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References and Notes

(1) (a) University of Leuven; (b) State University of New York.

(2) B. De Groof, M. Van Beylen, and M. Szwarc, *Macromolecules* **8**, 396 (1975).

(3) A. I. Khol'kin, *Chem. Abstr.*, **79**, 105397u (1974).

(4) J. C. Favier, M. Fontanille, and P. Sigwalt, *Bull. Soc. Chim. Fr.*, 526 (1971).

(5) B. I. Nachmanovich, A. M. Sakharov, and A. A. Arest-Yakobovich, *Dokl. Akad. Nauk SSSR*, **212**, 900 (1973).

(6) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

(7) Note that the molecular weight distribution of any mixture of living and dead polymers used in our studies is the same as that of a corresponding mixture of BaS_2 and BaB_2 of the same specific viscosity. Therefore, the method used in determining K_a is justified for *any* molecular weight distribution.

(8) This inequality follows from the intuitively obvious requirement, namely equilibrium constant $K_{i,ex}$ for $(BaB)^+ + S^- \rightleftarrows (BaS)^+ + B^-$ should be much greater than 1. Note that $K_b/K_c = K_{i,ex}$.

Synthesis and Polymerization of Some New Carbazole and Phthalimide Monomers

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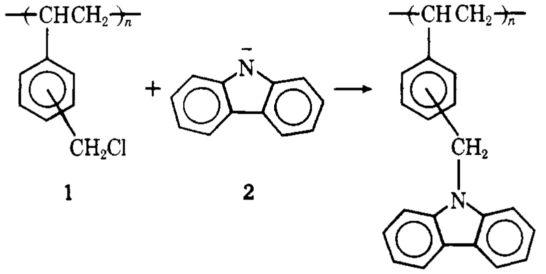
ABSTRACT: *m*- and *p*-(*N*-carbazyl)methylstyrenes and *p*-(*N*-phthalimido)methylstyrene were synthesized by reaction of a mixture of *m*- and *p*-chloromethylstyrene with potassium carbazole and potassium phthalimide, respectively. These polymerize and copolymerize readily with AIBN initiation to medium molecular weights. The resultant polymers are very similar spectrally to the analogous polymers made by chemical modification of poly(vinylbenzyl chloride).

Our interest in chemical modification of polymers led us to apply this method to the synthesis of poly[(*N*-carbazyl)methylstyrene] (**3**) from poly(vinylbenzyl chloride) (**1**) and the anion (**2**) of carbazole.[1] Polymer **1** was a mixture of isomers (60% meta, 40% para according to the manufacturer (Dow Chemical Co.) of the starting monomer) and, therefore, product polymer **3** was also a mixture of isomers inasmuch as the conversion was 100%. A synthesis of the two individual isomers of polymer **3** seemed desirable to ascertain any differences between the two isomers and corroborate the structure of **3**.



1 2 3

This undertaking is reported here.

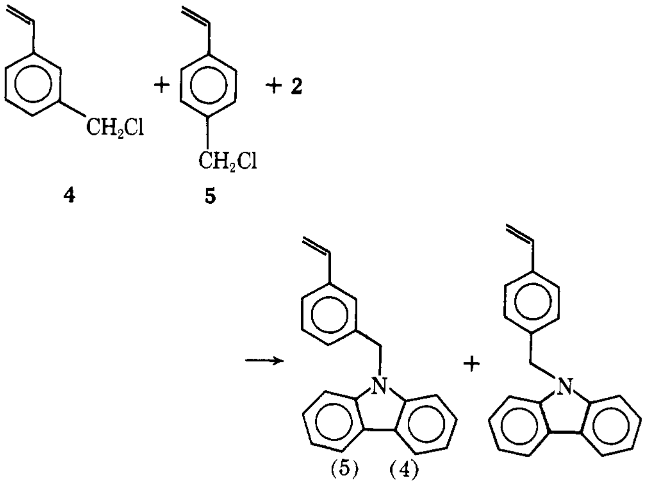
Discussion

(A) Synthesis of Monomers. A mixture of *m*-chloromethylstyrene (**4**) and the para isomer **5** in 60:40 nominal ratio was available (Dow Chemical Co.). Following the same procedure used for the preparation of polymer **3**,[1] reaction of a mixture of **4** and **5** with potassium carbazole (**2**) led to a mixture of the desired carbazole-containing monomers **6** and **7**. Fractional crystallization of the product mixture from ethanol led to a 29% yield of the less soluble para isomer **7** and a 64% yield of the more soluble meta isomer **6**; the total recovered conversion was therefore 93%. Separation is facile on account of a tenfold difference in the solubilities of the two isomers. The infrared and NMR spectra support the structural assignments.

The ultraviolet spectra of **6** and **7** are very similar to **3** and *N*-ethylcarbazole. Bands below 285 nm do not match in **3** and the monomers, presumably due to the vinyl group in the latter. Below 290 nm the extinction coefficients for **7** are higher than those of **6**.

Reaction of phthalimide anion with the mixture of chloromethylstyrenes (**4** and **5**) by the K_2CO_3/DMF method[1] led to 52% crude yield of solid, from which was isolated *p*-(*N*-phthalimido)methylstyrene (**8**). The lower melting, more soluble meta isomer was not isolated in a pure state. Infrared and NMR spectra are consistent with these assignments.

(B) Polymerization of Vinyl Monomers. Monomers **6**, **7** and **8** were each homopolymerized to polymers **9–11**, respectively, under free-radical conditions (azobisisobutyronitrile (AIBN) initiation) in refluxing benzene. Conversions



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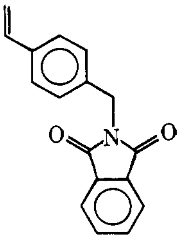

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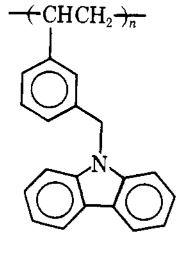

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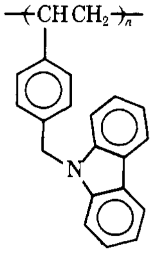

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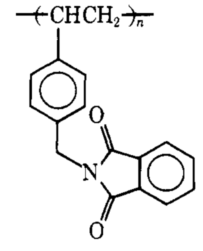

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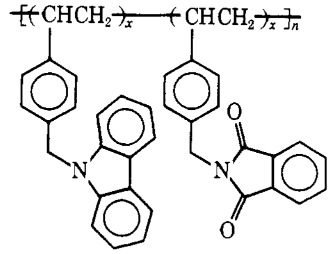

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ranged from 62 to 79%. The polymers were soluble in benzene, tetrahydrofuran (THF), chloroform, etc.

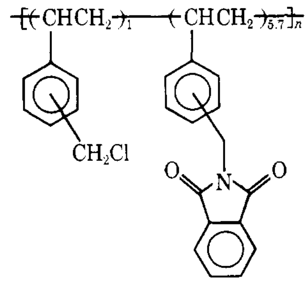
Monomers 7 and 8 were similarly copolymerized using a 1:1 charge ratio. Conversion was 61%. Elemental analysis indicates a 1:1 copolymer, i.e., 12, suggesting that the reactivities of the two monomers are quite similar.

Molecular weight data were obtained by gel permeation chromatography (GPC). As expected these monomers polymerize readily under these conditions to medium molecular weights.

(C) Spectral Characterization of the Polymers. The infrared spectra of the polymers 9 and 10 differ discernibly only in the presence of a peak at 885 cm^{-1} (isolated aromatic C–H bend[2]) for 9 and the presence of peaks at 800, 990, and 1010 cm^{-1} (two adjacent aromatic C–H bends[2]) and at 1415 cm^{-1} for 10 and the presence of a C=C at 1625 cm^{-1} in 9 and 1618 cm^{-1} in 10. The spectrum of 3 prepared from 1 is identical with that of 9 except that the 885-cm^{-1} peak is less intense and the presence of peaks at 990, 1020, 1418, and 1615. On the basis of the 1615 and 1625 C=C peaks the polymer 3 is 35 ± 5% para. This confirms the assumed isomer ratios of 1 and 3.[1]

The ultraviolet spectra of 9 and 10 reflect the same differences in extinction coefficients observed with monomers 6 and 7, namely slightly lower (<10%) ϵ's for the meta polymer 9 below 270 nm. In general, the spectra of 9 and 10 are very similar to that of 3.

The infrared spectra of 11 and the analogous 13 derived from 1[1] are virtually identical, the main features being the carbonyl peaks at 1720 and 1780 cm^{-1}.



13

The infrared spectrum of copolymer 12 is a composite of the spectra of 10 and 11; there are no new absorptions. Likewise the ultraviolet spectrum of 12 shows no new absorptions. This is in contrast to copolymers of *N*-vinylcarbazole and *N*-vinylphthalimide which possess a "charge-transfer" absorption at ~400 nm.[3] However, the effect of decreasing the molar percentage of carbazole moieties in the polymer on the extinction coefficients[1] is clearly seen in the wavelengths above 300 nm where there are no phthalimide absorptions; the extinction coefficients based on the carbazole moiety are 7% higher for 343 nm, 13% higher for 328 nm, and 37% higher for the 318 nm shoulder of 12 relative to 9. These results again suggest that in 9 interaction of the carbazole groups occurs. Thus, while charge-transfer interactions between carbazole and phthalimide groups were not detected, the previously described[1] dependence of extinction coefficient upon polymer composition was substantiated. The present data do not fall on the curves previously reported,[1] presumably because the present copolymer is comprised solely of para-substituted monomers, whereas the earlier data referred to mixtures of meta and para isomers.

Summary

m- and *p*-(*N*-carbazyl)methylstyrenes and *p*-(*N*-phthalimido)methylstyrene were synthesized by reaction of a mixture of *m*- and *p*-chloromethylstyrene with potassium carbazole and potassium phthalimide, respectively. These polymerize and copolymerize readily with AIBN initiation to medium molecular weights. The resultant polymers are very similar spectrally to the analogous polymers made by chemical modification of poly(vinylbenzyl chloride).

Experimental Section

General. All melting points (Thomas-Hoover apparatus, open capillaries) are corrected. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. NMR spectra were obtained on a Jeolco C-60H unit at 25 °C; chemical shifts are relative to tetramethylsilane. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer Model 283 spectrometer and are reported in reciprocal centimeters. Ultraviolet spectra were recorded on a Cary Model 15 instrument using matched cells and concentrations of 2–6 $\times 10^{-4}$ M in spectrograde solvents; spectra are presented as λ_{max} in nanometers ($\epsilon \times 10^{-3}$). GPC analyses were carried out on a Waters Model 200 chromatograph on 0.025 wt % solutions in tetrahydrofuran (THF); molecular weights are in polystyrene equivalents since the "Q factors" for these polymers are unknown.

***m*- and *p*-(*N*-Carbazyl)methylstyrenes (6 and 7).** This reaction was carried out by the same procedure as for preparation of **3**[1] using a nominal 60/40 mixture of *m*- and *p*-vinylbenzyl chlorides (**4** and **5**) (Dow experimental monomer XD19152). The reaction mixture was poured into water. Fractional recrystallizations from ethanol led to 29% of the less soluble isomer **6** as fine colorless needles, mp 174.0–174.5 °C. Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.65; H, 6.06; N, 5.08. NMR ($CDCl_3$)δ: 5.05–5.88 (m, 2 H, $=CH_2$), 5.45 (s, 2 H, $N—CH_2$), 6.4–6.8 (m, 1 H, CH=), 7.0–7.5 (m, 10 H, arom), 8.1–8.2 (m, 2 H, H_4, H_5). IR: 1910 (para-disubstituted benzene[2]), 820 (para-disubstituted benzene[2]), 735 (ortho-disubstituted benzene[2]). UV (CH_3OH): 341 (4.33), 327 (3.69), 317 sh (2.4), 293 (17.9), 287 (12.4), 282 sh (11.1), 258 (32.9), 246 sh (41.2), 236 (53.2).

The more soluble isomer **6** was obtained in 64% yield as nearly colorless stout needles (*n*-hexane), mp 66.5–68.0. Anal. Calcd. for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.11; H, 6.02; N, 4.97. NMR ($CDCl_3$)δ: 4.95–5.65 (m, 2, H, $=CH_2$), 5.18 (s, 2 H, $N–CH_2$), 6.25–6.8 (m, 1 H, $CH=$), 6.9–7.5 (m, 10 H, arom), 7.95–8.15 (m, 2 H, H_4, H_5). IR: 1890 (meta-disubstituted benzene[2]), 797, 882 (meta-disubstituted benzene[2]), 735 (ortho-disubstituted benzene[2]). UV (CH_3OH): 341 (4.40), 327 (3.73), 317 sh (2.3), 293 (19.9), 287 sh (11.7), 282 sh (9.83), 258 (2.81), 241 sh (29.2), 236 (41.8).

***p*-(*N*-Phthalimido)methylstyrene (8).** Reaction to 60:40 mixture of **4** and **5** (Dow Chemical Co.) and phthalimide using K_2CO_3/DMF as in the analogous polymer reaction[1] led to a 52% yield of a crude solid. Four recrystallizations from ethanol gave **8** as colorless fluffy crystals, mp 99.0–100.0 °C. Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.52; H, 5.02; N, 5.26. NMR ($CDCl_3$) δ: 4.75 (s, 2 H, NCH_2), 5.03–5.80 (m, 2 H, $=CH_2$), 6.37–6.85 (m, 1 H, $CH=$), 7.13–7.80 (m, 8 H, arom). IR: 832 (para-disubstituted benzene[2]), 739 (ortho-disubstituted benzene[2]), 1705, 1760 (C=O). The meta isomer present in the product mixture was more soluble and lower melting (~60 °C); it was not isolated in a pure state. IR: 760, 819, 850 (meta-disubstituted benzene[2]), 832 (weaker, para-disubstituted benzene[2]), 739 (ortho-disubstituted benzene[2]), 1710, 1760 (C=O).

Polymerization of Vinyl Monomers. A solution of 3.5 mmol of monomer(s) and 12 ml of dry benzene was purged with dry nitrogen for 20 min. Then 7 mg (0.04 mmol) of AIBN in 2.5 ml of dry benzene was added. The solution was refluxed for 16 h under dry nitrogen and then added dropwise to 200 ml of rapidly stirred methanol. The polymer was isolated by filtration, weighed to give conversion, and purified by three more precipitations from THF into methanol. From the original methanol filtrate unreacted monomer(s) was (were) recovered.

Poly[*m*-(*N*-carbazyl)methylstyrene] (9). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05. Found: C, 88.23; H, 5.82. IR: 885 (meta-disubstituted benzene[2]), 1625 (weak, C=C). UV (THF): 344 (4.61), 330 (4.16), 318 sh (2.76), 295 (16.5), 290 sh (11.3), 284 (9.71), 262 (19.6), 246 sh (26.9), 237 (40.8), 230 (39.2). GPC: $\overline{M}_n = 11.0 \times 10^3$, $\overline{M}_w = 19.4 \times 10^3$, MWD = 1.75.

Poly[*p*-(*N*-carbazyl)methylstyrene] (10). Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05. Found: C, 89.01; H, 6.01. IR: 800, 990, 1010 (para-disubstituted benzene[2]), 1415 (?), 1618 (weak, C=C). UV (THF): 344 (4.53), 330 (4.02), 318 sh (2.76), 275 (16.0), 290 sh (11.1), 284 sh (9.24), 262 (19.7), 246 sh (27.4), 237 (41.2), 230 (44.4). GPC: $\overline{M}_n = 9.69 \times 10^3$, $\overline{M}_w = 24.4 \times 10^3$, MWD = 2.51.

Poly[*p*-(*N*-phthalimido)methylstyrene] (11). Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98. Found: C, 77.28; H, 4.93. IR: 1710, 1770 (C=O). UV (THF): 300 sh (1.82), 293 (2.03), 253 sh (1.66), 240 sh (11.1). GPC: $\overline{M}_n = 8.63 \times 10^3$, $\overline{M}_w = 14.4 \times 10^3$, MWD = 1.70.

Poly[*p*-(*N*-carbazyl)methylstyrene-*co*-*p*-(*N*-phthalimido)methylstyrene] (12). Anal. Calcd for $C_{21}H_{17}N \cdot C_{17}H_{13}NO_2$: C, 83.49; H, 5.53; N, 5.12. Found: C, 82.97; H, 5.24; N, 5.05. IR: 1710, 1770 (C=O). UV (THF, ϵ based on carbazole): 344 (4.93), 330 (4.70), 318 sh (3.79). GPC: $\overline{M}_n = 7.28 \times 10^3$, $\overline{M}_w = 15.1 \times 10^3$, MWD = 2.03.

References and Notes

(1) H. W. Gibson and F. C. Bailey, *Macromolecules*, **9**, 688 (1976).

(2) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif., 1962, pp 24–27.

(3) W. W. Limburg and D. A. Seanor, U.S. Patent 3 877 936, assigned to Xerox Corp.

Synthesis and Characterization of Poly(styrene-*g*-isoprene) Copolymers

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ABSTRACT: Poly(styrene-*g*-isoprene) copolymers have been prepared by a modification of the standard chloromethylation process. The active CH_2Cl sites on the backbone were converted to $CH_2OSi(CH_3)_2Cl$ groups before coupling with polyisoprenyllithium. More quantitative coupling is obtained in this way. The graft copolymers produced were studied in solution in several solvents by light scattering and intrinsic viscosity techniques. It was found that such graft copolymers have a much less segregated structure in solution than do the corresponding two-block copolymers. The changes in intrinsic viscosity produced by adding side chains of increasing length can be roughly predicted in terms of a compositional and a branching effect.

Despite the many efforts that have been put into the preparation of well-characterized, homogeneous, narrow molecular weight distribution comb polymers, a completely satisfactory method has not yet been developed. A detailed study of the effect of branching on physical properties requires, if possible, a quantitative coupling reaction. In this way, a series of polymers of varying branch length with a constant number of branches on a given backbone can be prepared. The series can be completed if necessary by repetitions using different backbones. Most workers have recognized that the direct coupling of polystyrylpotassium with chloromethylated polystyrene gives the best results. However, the substitution reaction is accompanied by backbone–backbone coupling as a result of metal–halogen exchange, leading to comb polymers of higher than the theoretical molecular weight. At the same time, incomplete substitution produces less than the theoretical number of branches in these combs.[2–4] In order to attain the objectives outlined above and to increase the probability of obtaining more homogeneous products, both difficulties have to be overcome. The reaction of low molecular weight chlorosilane compounds with polystyryllithium and polyisoprenyllithium is known to produce regular star-branched polymers without complicating side reactions.[5–7] The same reaction has been applied to the preparation of comb polystyrenes[8] with less success. No satisfactory explanation could be given for the fact that only about 70–80% of the theoretical number of branches was found in the comb polymers. In addition, the molecular weight distributions of the graft copolymers were wider than is desirable. This was only partly caused by starting from backbone poly-