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Table I
 $V_g^{(P)cor}/V_g^{(P)unc}$ for *n*-Alkane Retentions^a on
Three Polymers

probe	PVA	PECH	PCL
ethane	2.944	2.080	2.048
propane	1.660	1.391	1.357
butane	1.280	1.164	1.128
pentane	1.148	1.077	1.060
hexane	1.077	1.036	1.028
heptane	1.044	1.018	1.014
octane	1.025	1.009	1.007
nonane	1.015	1.004	1.003

^a PVA data at 110 °C; PECH and PCL data at 80 °C.

Table II
Flory-Huggins Interaction Parameters^a χ_{12} for *n*-Alkanes
with Three Polymers, Both with and without the
Marker Correction

probe	uncorrected data			corrected data		
	PVA	PECH	PCL	PVA	PECH	PCL
propane	1.682	1.651	1.267	1.167	1.325	.963
butane	1.589	1.660	1.123	1.339	1.511	1.003
pentane	1.665	1.722	1.202	1.526	1.649	1.143
hexane	1.684	1.754	1.218	1.610	1.719	1.190
heptane	1.802	1.846	1.277	1.759	1.828	1.264
octane	1.916	1.945	1.351	1.891	1.936	1.344
nonane	2.056	2.051	1.424	2.041	2.047	1.421

^a PVA data at 110 °C; PECH and PCL data at 80 °C.

marker can be seen from the quantity $V_g^{(P)cor}/V_g^{(P)unc}$ for the alkane probes, which is listed in Table I for the three polymers. Here $V_g^{(P)cor}$ and $V_g^{(P)unc}$ designate respectively the corrected and uncorrected specific retention data. The table demonstrates that even for a well-retained probe like *n*-octane an error of over 2% in $V_g^{(P)}$ and $V_n^{(P)}$ can be introduced by failure to account for the marker. The magnitude of this error will obviously depend on the polymer, probe, and temperature, but, ideally, it should not depend on the extent of polymer loading since the marker and the probes are equally affected by a change in polymer mass. The corrected specific retention data for the three polymers are shown on the right-hand axis of Figure 1 to further illustrate this point. The retentions of the various probes on PVA are comparable to those on PECH but the lower slope of the PVA line suggests a higher value for the ratio $V_g^{(P)cor}/V_g^{(P)unc}$.

The errors incurred in the values of $V_g^{(P)}$ from ignoring the retention of methane are carried into the calculation of the probe-polymer interaction parameter. In IGC studies on polymers, the Flory-Huggins interaction parameter χ_{12} is the routine choice for reporting such interactions.⁷⁻⁹ In Table II, χ_{12} for the three polymers is listed for the *n*-alkanes C₃-C₉. The values of χ_{12} are given both with and without the marker correction. As expected, the correction is most important for the least retained probe, propane, and remains significant even for the high alkanes. The error introduced by the conventional analysis is most pronounced for PVA and is smaller for PECH and PCL.

In conclusion, the marker correction procedure explained above significantly improves the quality of IGC data and allows a more meaningful analysis and comparison of data from different IGC experiments.

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Registry No. PVA, 9003-20-7; PECH (homopolymer), 24969-06-0; PECH (SRU), 61710-61-0; PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; ethane, 74-84-0; propane,

74-98-6; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; nonane, 111-84-2; methane, 74-82-8.

References and Notes

- (1) Peterson, M. L.; Hirsch, J. J. *Lipid Res.* **1959**, *1*, 132-134.
- (2) Guardino, X.; Albaiges, J.; Firpo, G.; Rodriguez-Vinals, R.; Gassiot, M. *J. Chromatogr.* **1976**, *118*, 13-22.
- (3) Garcia Dominguez, J. A.; Garcia Munoz, J.; Fernandez, S. E.; Molera, M. J. *J. Chromatogr. Sci.* **1977**, *15*, 520-527.
- (4) Smith, J. M.; Haken, J. K.; Wainwright, M. S.; Madden, B. G. *J. Chromatogr.* **1985**, *328*, 11-34.
- (5) Conder, J. R.; Young, C. L. *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1979; pp 91-92.
- (6) Al-Saigh, Z. Y.; Munk, P. *Macromolecules* **1984**, *17*, 803-809.
- (7) *Pyrolysis and GC in Polymer Analysis*; Liebman, S. A.; Levy, E. J., Eds.; Chromatographic Science Series 29; Marcel Dekker: New York, 1985; pp 411-412.
- (8) DiPaola-Baranyi, G.; Guillet, J. E. *Macromolecules* **1978**, *11*, 228-235.
- (9) Schuster, R. H.; Grater, H.; Cantow, H. *Macromolecules* **1984**, *17*, 619-625.

Reactions of *n*-Type (Reduced) Polyacetylene with Alkyl Halides¹

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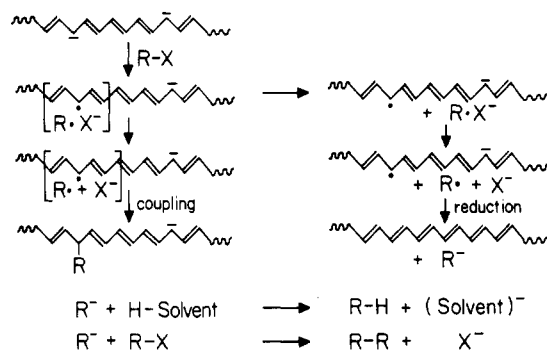
The reactions of charge carriers (typically carbenium ions or carbanions) in "doped"⁴ conductive polymers with various reagents⁵ can be a major limitation to technological applications as well as a useful approach for the synthesis of new materials,⁷ although very little is known about reaction mechanisms. Of particular interest is whether the carriers may act as oxidants/reductants or acids (or electrophiles)/bases (or nucleophiles)⁸ and under what conditions one mechanism may predominate. We have elected to study the reactions of *n*-type (reduced) polyacetylene,⁹ [(CHNa)_x or *n*-PA, with alkyl halides due to the extensive literature on similar reactions with small molecule radical anions¹⁰ and dianions.¹¹ Our experiments suggest that extensive alkylation of *n*-PA occurs and proceeds by initial electron transfer to R-X followed by radical coupling (Scheme I) and that the reactivity patterns of various alkyl halides (Table I) parallel those observed with disodium tetraphenylethylene (TPE).^{11a,b} Furthermore, we find that this chemistry provides a versatile route to the preparation of modified polyacetylenes having interesting physical properties.

Treatment of *n*-PA films¹² with, for example, 1-bromopentane in dry THF leads to alkylation of the PA¹⁴ to a level of ca. one *n*-C₅/ten CH units (Table I). Interestingly, the film swells considerably as the reaction proceeds and the THF solution becomes yellow-orange (λ_{max} ca. 380 nm) and slightly viscous, indicating the presence of a soluble, conjugated polymer.¹⁴ Several observations support the reaction mechanism^{11a,b} outlined in Scheme I wherein an alkyl radical,¹⁵ initially formed by electron transfer from *n*-PA, can either couple with a PA radical or undergo reduction to the corresponding carbanion.¹⁷ That the first step is an electron transfer rather than a nucleophilic attack is suggested by the detection of reduction products and the observation that a tertiary alkyl chloride (entry 10) reacts even faster with *n*-PA than a corresponding primary substrate (entries 1,2) and affords nearly the same extent of alkylation. Reactions with primary alkyl chlorides consume only ca. 50% of substrate,

Table I
Products of the Reaction of n-PA with Selected Alkyl Halides
[CH(Na)_y]_n → [CH(R)_z]_n

entry	reactant (RX)	y	z ^e	% reacted, [I] ^c	% (RH + RR), [II] ^c	% R(alkylation), [III] ^e	(II + III)/I ⁱ
1	CH ₃ (CH ₂) ₄ Cl	0.27	0.12 ^f	53	5 ^d	80 ^f	85
2	CH ₃ (CH ₂) ₄ Cl	0.25	0.12 ^f	48	8 ^d	88 ^f	96
3	CH ₃ (CH ₂) ₄ Br	0.26	0.14 ^g	76	11 ^d	72 ^{f,g}	83
4	CH ₃ (CH ₂) ₄ Br	0.21	0.12	76	15	77	92
5	CH ₃ (CH ₂) ₄ Br	0.24	0.14 ^b	78	12 ^d	75 ^f	87
6	CH ₃ (CH ₂) ₄ Br	0.19	0.13	75	11	87	98
7	CH ₃ (CH ₂) ₇ Br	0.28	0.14	70	15	83	98
8	CH ₃ (CH ₂) ₁₁ Br	0.26	0.14 ^g	82	13 ^d	73 ^g	86
9	CH ₃ (CH ₂) ₁₁ Br	0.24	0.15	75	13	83	96
10	(CH ₃) ₃ CCl	0.27	0.12	77	19	61 ^f	80
11	CH ₃ (CH ₂) ₄ I	0.25	0.11 ^f	74	22	62 ^f	84
12	CMTMS ^a	0.23	0.015 ^g	43	88 ^b	2 ^g	90

^a CMTMS = (chloromethyl)trimethylsilane. ^b CPTMS = (chloropropyl)trimethylsilane. ^c Amount of substrate consumed, based on a 1:1 substrate/carbanion stoichiometry, determined by GC. ^d Neglecting dimer (R-R) formation. ^e Based on amount of substrate consumed, determined gravimetrically unless otherwise noted. ^f Neglecting weight and composition of soluble fraction (typically 5–10 wt%). ^g Determined by elemental analysis. ^h Determined from ¹H NMR integration^{17b} of a reaction run in THF-d₈. ⁱ Mass balance.

Scheme I^a

^a Counterions omitted for clarity. Large brackets indicate cages.

consistent with the fact that such halides are the most difficult to reduce¹⁸ (of those listed in Table I) and that the reducing power of n-PA decreases as the carrier (carbanion) concentration decreases.¹⁹ Our contentions are further supported by the observation that treatment of n-PA with (chloromethyl)trimethylsilane (entry 12), which is known to undergo nucleophilic displacement more quickly^{20a} than 1-chloroalkanes, results in little alkylation of PA although the amount of substrate consumed is approximately the same as that when 1-chloropentane is employed. Rather, most of the silane is converted to reduction products^{20b} (see Table I), suggesting that the intermediate radical is quickly reduced to the carbanion which is reasonable based on the known tendency of Si to stabilize α -carbanions.^{20c} When Si cannot participate in such stabilization (entry 13), an amount of alkylation comparable to that derived from reactions with 1-chloropentane is observed.

We find that the amount of reduction products increases for primary halide substrates as a function of halide in the order $\text{I} > \text{Br} > \text{Cl}$ as has been reported^{11a} for similar reactions with TPE²⁻, presumably attributable to the relative stabilities of R^+X^- ; the latter is most stable,^{11b} and therefore is more likely to diffuse away from the initially formed n-PA radical/ R^+X^- pair, when $\text{X} = \text{I}$. Thus, reduction to R^- (affording reduction products by reaction with protons from solvent and/or R-X) can more effectively compete with alkylation (via radical coupling) of n-PA. These ideas can also explain the relative insensitivity of the amount of PA alkylation to R-X structure (with the exception of entry 12, vide supra) since, although primary bromides and

iodides exhibit greater extents of reaction compared with chlorides, more of the former two are consumed in the generation of reduction products (presumably via R^-).²¹

The alkylated PA films exhibit desirable properties (e.g., solvent swellability and elasticity) which are dependent on the alkyl structure. For example, PA alkylated with $n\text{-C}_5$ groups is somewhat flexible at room temperature and is elastic when wetted with pentane, while films alkylated with $n\text{-C}_{12}$ are very elastic even when dry. Also, the films possess reasonably long conjugation lengths considering that, on average (see Table I), there is roughly one alkyl group per ca. ten CH units.²² It should be noted that the chemistry discussed above can be used to attach a much wider variety of functional groups to PA (e.g., alcohols) provided that these groups are suitably protected during the reaction with n-PA. A detailed study of the physical, optical, and electrical properties of these novel materials is in progress and will be presented in a future paper.

Registry No. PA, 25067-58-7; CMTMS, 2344-80-1; CPTMS, 111113-79-2; $\text{H}_3\text{C}(\text{CH}_2)_4\text{Cl}$, 543-59-9; $\text{H}_3\text{C}(\text{CH}_2)_4\text{Br}$, 110-53-2; $\text{H}_3\text{C}(\text{CH}_2)_7\text{Br}$, 111-83-1; $\text{H}_3\text{C}(\text{CH}_2)_{11}\text{Br}$, 143-15-7; $(\text{CH}_3)_3\text{CCl}$, 507-20-0; $\text{H}_3\text{C}(\text{CH}_2)_4\text{I}$, 628-17-1.

References and Notes

- (1) Supported by a grant from the Office of Naval Research and a an ARCO Career Development Award (to G.E.W.).
- (2) Present address: Polaroid Corporation, Cambridge, MA 02139.
- (3) Present address: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590.
- (4) The term "doped" refers to an oxidized or reduced form of the polymer backbone.
- (5) These include ambient species such as H_2O and O_2 ,^{6a,b} as well as electrolytes^{6c} in batteries and various monomers for grafting reactions.^{7b-d}
- (6) (a) Chung, T. C.; Feldblum, A.; Heeger, A. J.; MacDiarmid, A. G. *J. Chem. Phys.* **1981**, *74* (10), 5504. (b) Pron, A.; Faulques, E.; Lefrant, S. *Polym. Commun.* **1987**, *28*, 27. (c) See, for example: Reynolds, J. R.; Schlenoff, J. B.; Chien, J. C. W. *J. Electrochem. Soc.* **1985**, *132* (5), 1131.
- (7) (a) Shirakawa, H.; Sato, M.; Hamano, A.; Kawakami, S.; Soga, K.; Ikeda, S. *Macromolecules* **1980**, *13*, 457. (b) Dandreaux, G. F.; Galvin, M. E.; Wnek, G. E. *Org. Coat. Appl. Polym. Sci. Proc.* **1983**, *48*, 541. (c) Galvin, M. E.; Dandreaux, G. F.; Wnek, G. E. In *Polymers in Electronics*; Davidson, T., Ed.; ACS Symp. Ser. 242; American Chemical Society: Washington, DC, 1984; p 507. (d) Kminek, I.; Trekoval, J. *Makromol. Chem. Rapid Commun.* **1984**, *5*, 53. (e) Yaniger, S. I.; Kletter, M. J.; MacDiarmid, A. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*, 264. (f) Whitney, D. H.; Wnek, G. E. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 313. (g) Reaction of n-PA with, for example, ethylene oxide can improve the performance of the PA as a cathode material. See: Maxfield, M.; Wolf, J. F.; Miller, G. G.; Frommer, J. E.; Shacklette, L. W. *J. Elec-*

- trochem. Soc.* 1986, 133, 117. (h) For a description of catalytic properties of n-PA, see: Soga, K.; Ikeda, S. In *Handbook of Conducting Polymers*; Skotheim, T., Ed.; Marcel Dekker: New York, 1986; Chapter 18, pp 661-672.
- (8) Such a distinction has been criticized by Pross who encourages the idea that, for example, a so-called (single) electron transfer and a (two electron) nucleophilic attack both actually involve single electron shifts (see: Pross, A. *Acc. Chem. Res.* 1985, 18, 212). For reasons of consistency with earlier literature,^{10,11} we will continue to employ this distinction.
- (9) The charge carriers are believed to be delocalized carbanions (pairs of which are referred to as bipolarons) formed by intramolecular radical recombination of radical anions. See: Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* 1985, 18, 309.
- (10) Garst, J. F. *Acc. Chem. Res.* 1971, 4, 400.
- (11) (a) Garst, J. F.; Roberts, R. D.; Pacifici, J. A. *J. Am. Chem. Soc.* 1977, 99, 3528. (b) Symons, M. C. R. *J. Chem. Res., Synop.* 1978, 360.
- (12) The n-PA was prepared by immersion of PA films^{13a} in 0.5 M sodium naphthalide in THF for 24-48 h followed by washing with dry THF until the washings were colorless. All operations were carried out in a glass apparatus^{13b} which was previously flame dried on a vacuum line. The compositions of the "doped" films were determined by gravimetric analysis and were occasionally cross-checked by treatment with MeOH followed by titration of the supernatant with standardized HCl.
- (13) (a) The procedure for the synthesis of PA films can be found in: Chien, J. C. W. *Polyacetylene: Chemistry, Physics and Material Science*; Academic: New York, 1984; p 25-34. Occasionally, C₂D₂ (from Li₂C₂ and D₂O) was polymerized and the resulting deuteriated PA was used in our experiments in order to confirm the extent of alkyl (nondeuteriated) incorporation¹⁴ by IR spectroscopy. (b) Reference 13a, p 327.
- (14) All reactions were carried out in a drybox. As an example, ca. 100 mg of n-PA film having a composition [CH(Na)_{0.20}]_x (1.1 mmol charge carriers) in 5 mL of dry THF in a screw-cap vial was treated with 0.165 mL (1.3 mmol) of 1-bromopentane for 24 h. Both the resulting swellable film and soluble fraction contain n-pentyl groups as indicated by IR spectra of samples prepared from deuteriated PA. The amounts of substrate consumed and reduction products (Scheme I) formed were determined by GLC. The extents of alkylation were determined by elemental analysis (Schwartzkopf Laboratories, Woodside, NY).
- (15) The intermediacy of radicals is inferred from the experimental data (see text). An experiment employing 6-bromo-1-hexene afforded PA containing terminal olefins (IR spectroscopy) and, as reduction products, 1-hexene and methylcyclopentane in a 5:1 ratio. The formation of methylcyclopentane suggests the intermediacy of 1-hexenyl radicals.¹⁸ The greater amount of 1-hexene is likely due to the high local concentration of reducing species in n-PA films in these heterogeneous reactions, and thus reduction of 1-hexenyl radicals competes with cyclization. In fact, Garst et al.¹⁸ found that 1-hexene is the major reduction product when 6-bromo-1-hexene is treated with excess sodium naphthalide radical anion.
- (16) Garst, J. F.; Ayers, W. P.; Lamb, R. C. *J. Am. Chem. Soc.* 1966, 88, 4260.
- (17) Group I alkyls (e.g., n-BuLi) are able to dope polyacetylene to n-PA. See: (a) Francois, B.; Mathis, C.; Nuffer, R.; Rudatikira, A. *Mol. Cryst. Liq. Cryst.* 1985, 117, 113. (b) Elsenbaumer, R. L.; Miller, G. G.; Toth, J. E. U. S. Patent 4 526 708, July 2, 1985. This is not inconsistent with our contention that alkyl carbanions can be produced from n-PA by reduction of alkyl radicals since in our experiments the alkyl carbanion concentration is small relative to the concentration of n-PA carbanions. (The opposite situation exists in doping.^{17a,b})
- (18) (a) Lambert, F. L. *J. Org. Chem.* 1966, 31, 4184. (b) Lambert, F. L.; Ingall, G. B. *Tetrahedron Lett.* 1974, 36, 3231. (c) Alkyl fluorides are expected to be even more difficult to reduce and in fact no reaction of n-PA with 1-fluoropentane occurred over a period of 3 days as indicated by the observation that the electrical conductivity of the n-PA decreased by only a factor of 2. On the contrary, *tert*-butyl chloride is easier to reduce^{18b} and consequently the extent of reaction with n-PA (Table I) is greater than that with 1-chloropentane.
- (19) The reduction potential of n-PA varies from -2.8 to -2.05 V versus SCE for dopant compositions from ca. 10% to ca. 0.01%, respectively. See: MacDiarmid, A. G.; Kaner, R. B. In *Handbook of Conducting Polymers*, Skotheim, T., Ed.; Marcel Dekker: New York, 1986; Chapter 20, p 696.
- (20) (a) Chvalovsky, V.; Bellama, J. M. *Carbon-Functional Organosilicon Compounds*; Plenum: New York, 1984; pp 76-77. (b) The material balance in Table I is based on the amount of tetramethylsilane, 1,2-bis(trimethylsilyl)ethane, and bis(trimethylsilyl)methane detected by NMR. While these are also the major products in the reaction of CMTMS with sodium, lesser amounts of other products have been reported. See: Connolly, J. W.; Urry, G. J. *Org. Chem.* 1964, 29, 619. (c) Boak, D. S.; Gowenlock, B. G. *J. Organomet. Chem.* 1971, 29, 385.
- (21) It is interesting to compare the reactions of n-PA and another heterogeneous reactant, C₆K (K-intercalated graphite or n-type graphite); the amount of alkylation in the latter is not greater than 5%. See: Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* 1978, 100, 2126.
- (22) The compositions suggest that, on average, there are four C=C bonds in conjugation between the alkylated (presumably sp³) carbons. However, the alkylated films have a similar appearance to PA and the λ_{max} of an alkylated film (grown as a thin film on NaCl and then reduced and alkylated) is ca. 620 nm, a value quite inconsistent with tetraenes. These materials are presently being characterized in detail.

Amorphous Phase Segregation in Polyethylene-Based Ionomers

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Introduction

"Ionomer" is a generic term for copolymers of an olefin (ethylene, butadiene, styrene, etc.) with a carboxylic monomer (acrylic acid, methacrylic acid, etc.) which have been neutralized, the H⁺ ions being replaced by other cations (Na⁺, Zn²⁺, etc.). Ionomer materials have been the subject of extensive studies over the last 2 decades. The morphology of ionomers is more or less understood at present.¹⁻³ Accordingly, the general understanding is that in a medium of low dielectric constant (e.g., hydrocarbon chains) the ions form aggregates. At lower ion contents, the ions aggregate to form multiplets, i.e., small aggregates (several ion pairs). At higher ion concentrations, many ions along with some nonionic material give rise to sizeable clusters which act not only as cross-links but more like microcrystallites.

The literature⁴⁻⁶ reveals that the T_g of ionomers increases with an increase in cation content, presumably due to a fairly uniform distribution of aggregates or clusters. Also documented is the existence of a double T_g ; one corresponding to the predominantly nonionic regions (i.e., unneutralized copolymer) and the other at higher temperature representing the predominantly ionic microphase.¹ Studies on ethylene (E)/acrylic acid (AA) copolymer salts by Otocka and Kwei reveal a regular increase in the T_g as a function of increasing ion content.⁷ Contrary to the generally accepted increase in T_g with ion content, a single reference has come to our attention in which MacKnight et al.⁸ suggest that the β -relaxation (or T_g) of an ethylene/methacrylic acid copolymer decreases upon neutralization while producing, simultaneously, a higher temperature relaxation.

In this note we present our independent results on the relaxation phenomenon in low molecular weight E/AA ionomers and support the observation of MacKnight et al.⁸ that in ethylene ionomers the main T_g decreases upon neutralization.