patterns corresponding to $d = 0.375$ nm indicates that they did not pack in an orthorhombic polyethylene fashion[14,19-22] but may resemble more closely the packing of the triclinic form[14,23] of polyethylene or the monoclinic form[20,21] of paraffins. At present we have insufficient information to make a decision on the possible resemblance to the triclinic or monoclinic forms of polyethylene and paraffins, the powder patterns of these forms being so similar to one another. The absence of measurable sharp reflections beyond the 0.4-nm region suggests[14] that the side chains are only packed regularly locally, and the regularity extends over limited lengths of the backbone, even though the backbones are well aligned to produce the sharp large-spacing, mobile peaks. This is, of course, in agreement with the suggestion that only parts (most likely, the remotest from the backbone) of the side chains are involved in side-chain crystallinity.

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References and Notes

(1) Aharoni, S. M. *Macromolecules* **1979**, *12*, 94.
(2) Aharoni, S. M.; Walsh, E. K. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 321.
(3) Aharoni, S. M.; Walsh, E. K. *Macromolecules* **1979**, *12*, 271.
(4) Aharoni, S. M. *Macromolecules* **1979**, *12*, 537.
(5) Aharoni, S. M. *Polymer* **1980**, *21*, 21.
(6) Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1439.
(7) Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1303.
(8) Aharoni, S. M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1980**, *21* (1), 209.
(9) Volchek, B. Z.; Nikitin, V. N. *Dokl. Akad. Nauk SSSR* **1972**, *205*, 622.
(10) Berger, M. N.; Tidswell, B. M. *J. Polym. Sci., Part C* **1973**, *42*, 1063.
(11) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976**, *76*, 727.
(12) Shmueli, U.; Traub, W.; Rosenheck, K. *J. Polym. Sci., Part A-2* **1969**, *7*, 515.
(13) Clough, S. B. In "Characterization of Materials in Research, Ceramics and Polymers"; Burke, J. J., Weiss, V., Eds.; Syracuse University Press: Syracuse, N.Y., 1975; pp 417-36.
(14) Turner Jones, A. *Makromol. Chem.* **1964**, *71*, 1.
(15) Balta-Calleja, F. J.; Ramos, J. G.; Barrales-Rienda, J. M. *Kolloid Z. Z. Polym.* **1972**, *250*, 474.
(16) Cubbon, R. C. P. *Polymer* **1965**, *6*, 419.
(17) Plate, N. A.; Shibayev, V. P. *Vysokomol. Soedin., Ser. A* **1971**, *13*, 410 (translated in *Polym. Sci. USSR* (*Engl. Transl.*) 1971, *13*, 466).
(18) Plate, N. A.; Shibayev, V. P. *J. Polym. Sci., Macromol. Rev.* **1974**, *8*, 117.
(19) Trafara, G.; Koch, R.; Blum, K.; Hummel, D. *Makromol. Chem.* **1976**, *177*, 1089.
(20) Trafara, G.; Koch, R.; Sausen, E. *Makromol. Chem.* **1978**, *179*, 1837.
(21) Trafara, G. *Makromol. Chem.* **1980**, *181*, 969.
(22) Blum, K.; Trafara, G. *Makromol. Chem.* **1980**, *181*, 1097.
(23) Turner Jones, A. *J. Polym. Sci.* **1962**, *62*, S53.

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Halato-Telechelic Polymers. 1. Gel Formation and Its Dependence on the Ionic Content

In the early 1960s, the du Pont de Nemours Co. commercialized the first ionomer material under the trade name Surlyn.[1] From that time, scientists have shown increasing interest in the behavior of this type on ion-containing polymer which consists of a lipophilic polymeric backbone carrying randomly distributed pendant ionic groups.[2-4] Ionomers are mainly characterized in bulk.[5-14] However, Joanny has theoretically studied the expected phase diagram of ionomers dissolved in a nonpolar solvent. Two phase transitions are expected: gelation and demixing.[15] In nonpolar solvents indeed, the ionic groups (usually carboxylate or sulfonate) are not dissociated but form electric dipoles, the attractive interaction of which can lead to their aggregation, i.e., gelation, and ultimately to the demixing of the system. The gelation was expected to vary inversely with the fraction of ionic groups along the chain.[15] Experimental data were therefore needed to give further insight into the behavior of ion-containing polymers in nonpolar solvents.

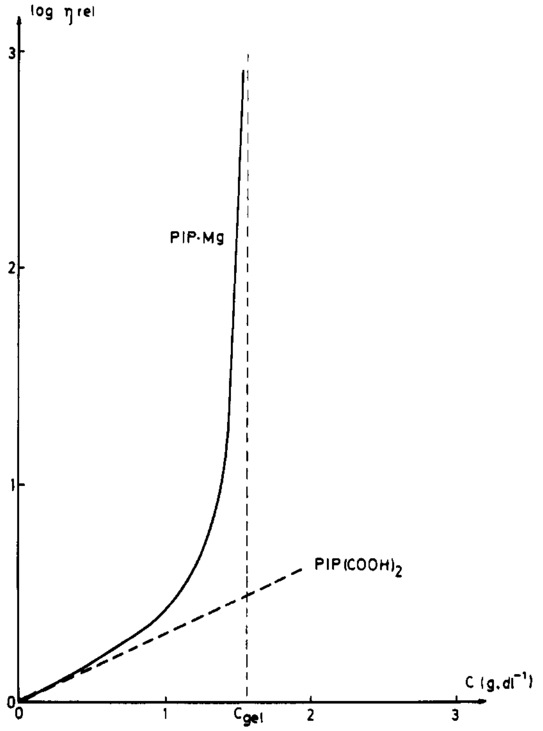
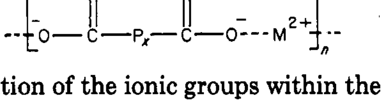


Figure 1. Relative viscosity (log scale) vs. concentration for carboxy-telechelic-PIP ($\bar{M}_n = 7 \times 10^4$) (---) and the same stoichiometrically neutralized with Mg^{2+} (—).

For this purpose, we have explored the synthesis of model-ionic polymers and, more especially, of halato-telechelic polymers (HTP). They are obtained from the complete neutralization of carboxy-telechelic polymers by alkaline-earth cations[16] and have the general formula



$$--\left[\overset{-}{O}-\overset{\overset{\displaystyle O}{\|}}{C}-P_x-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{O}---M^{2+}\right]_n--$$

The distribution of the ionic groups within the chain can largely be controlled by the length and the polydispersity of the prepolymer P_x. Previously, Otocka et al.[17] and Pineri et al.[18] were interested in similar materials, and aliphatic and aromatic dicarboxylic acid salts with a number of divalent cations have also been investigated.[19]

In the present work, carboxy-telechelic-polyisoprenes (PIP) with a good functionality (>1.95) and a low polydispersity ($\bar{M}_w/\bar{M}_n < 1.15$) were prepared anionically. The carboxylic acid end groups were neutralized in dry toluene by addition of a stoichiometric amount of magnesium methoxide. The methanol formed was completely displaced by azeotropic distillation of toluene under reduced pressure to ensure quantitative neutralization.

At high dilution in toluene, the magnesium α,ω-dicarboxylato-PIPs (denoted PIP-Mg) form homogeneous

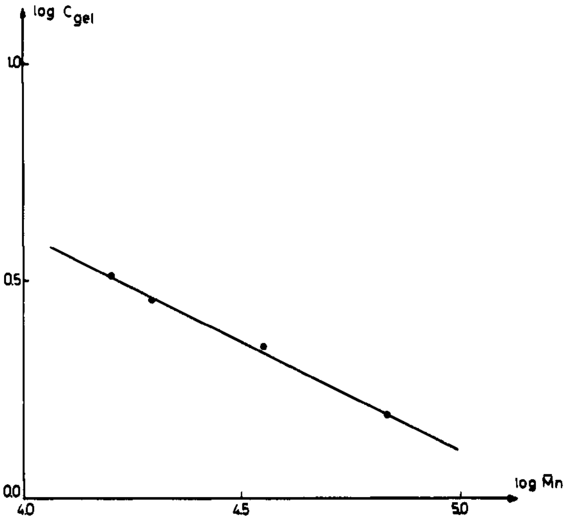


Figure 2. Gel concentration ($g{\cdot}dL^{-1}$) vs. PIP length ($\bar{M}_n$) (log-log plot) for magnesium α,ω-dicarboxylato-PIP in toluene at 25 °C.

fluid solutions, which suddenly gel upon increasing the concentration. Figure 1 clearly shows this behavior at 25 °C for a high molecular weight PIP-Mg ($\bar{M}_n$ of carboxy-telechelic-PIP = 7×10^4). At lower concentrations (<1%), the relative viscosity varies regularly as observed also for the nonneutralized PIP. At a given concentration, the influence of the ionic interactions takes over and promotes a sharp asymptotic increase of η_{rel}. The shape of this log η_{rel}-concentration plot (Figure 1) is characteristic of any HTP and expresses the occurrence of a cooperative gelation process. The vertical asymptote of this curve defines the critical gelation concentration (C_{gel}), i.e., the concentration necessary to aggregate the ionic groups and cross-link the difunctional PIP chains dissolved in toluene. The very low values of this C_{gel} (1-1.5 $g{\cdot}dL^{-1}$; see also Figure 2) are to be noted.

The relative viscosities were measured by a Desreux-Bisschoff capillary viscosimeter;[20] the shearing conditions were accordingly the same for each experimental determination. At constant PIP length ($\bar{M}_n = 7 \times 10^4$) and solvent (toluene), C_{gel} depends on the temperature in a perfectly reversible manner (1.54 $g{\cdot}dL^{-1}$ at 25 °C and 1.69 $g{\cdot}dL^{-1}$ at 50 °C). As reported elsewhere,[16] the greater the size of the divalent cation and the dielectric constant of the solvent, the higher the observed C_{gel}. All these experimental results agree with the dependence of C_{gel} on the electrostatic interactions between the nondissociated ionic groups in nonpolar solvents. It should be accordingly expected that C_{gel} decreases as the carboxylate content of PIP increases, in agreement with Joanny's prediction for ionomers.[15] To check the validity of this statement, C_{gel} has been experimentally related to the length of PIP, all other parameters being kept constant (Figure 2). The behavior of PIP-Mg in toluene at 25 °C is expressed by

$$C_{gel} = 407 \times M^{-0.5} \qquad (1)$$

where M is the molecular weight of the carboxy-telechelic-PIP. That means that C_{gel} varies inversely with PIP length or proportionally with the metal carboxylate content of PIP-Mg. It must also be noted that over the whole range of concentration (in toluene at 25 °C) no demixing of the PIP-Mg studied here (see Figure 2) was observed. There is, of course, disagreement between the experimental behavior of halato-telechelic polymers and Joanny's theory developed for ionomers.[15] Therefore, the aggregation process could be fundamentally different for these two types of ion-containing polymers, stressing the deep influence of the distribution of ionic groups along or within the polymeric backbone.

In conclusion, the aggregation of electric dipoles of HTP in nonpolar solvents is closely controlled by the molecular characteristics of the polymeric carrier, besides the well-known parameters of temperature, dielectric constant of the medium, and nature of the ionic group itself.

The validity of eq 1 is now being tested for polybutadiene and polyvinyl aromatic-based HTP, and a theoretical treatment is under study to explain satisfactorily the behavior observed. Information about the regularly organized morphology[21] and the particular rheology[22] of HTP will be reported soon.

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References and Notes

(1) E. I. du Pont de Nemours Co., Inc., U.S. Patent 3264272.
(2) Otocka, E. P. *J. Macromol. Sci., Rev. Macromol. Chem.* **1971**, *C5*, 275.
(3) Holliday, L., Ed. "Ionic Polymers"; Applied Science Publishers: London, 1975.
(4) Eisenberg, A.; King, M. "Polymer Physics"; Stein, R. S., Ed.; Academic Press: New York, 1977; Vol. 2.
(5) Rees, R. W.; Vaughan, D. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1965**, *6*, 287.
(6) Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
(7) Eisenberg, A. *J. Polym. Sci., Polym. Symp.* **1974**, *45*, 99.
(8) MacKnight, W. J.; Taggart, W. P.; Stein, R. S. *J. Polym. Sci., Polym. Symp.* **1974**, *45*, 113.
(9) Pineri, M.; Meyer, C.; Levelut, A. M.; Lambert, M. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 115.
(10) Eisenberg, A. *Contemp. Top. Polym. Sci.* **1979**, *3*, 231.
(11) Rouse, G. B.; Risen, W. M.; Tsatsas, A. T.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 81.
(12) Eisenberg, A.; Matsuura, M.; Tsutui, T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 479.
(13) Roche, E. J.; Stein, R. S.; MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1035.
(14) Earnest, T. R.; Higgins, J. S.; MacKnight, W. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1980**, *21*, 179.
(15) Joanny, J. F. *Polymer* **1980**, *21*, 71.
(16) Broze, G. Ph.D. Thesis, University of Liège, 1980.
(17) Otocka, E. P.; Hellman, M. Y.; Blyler, L. L. *J. Appl. Phys.* **1969**, *40*, 4221.
(18) Moudden, A.; Levelut, A.; Pineri, M. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 7707.
(19) Economy, J.; Mason, J. H. In ref 3, Chapter V.
(20) Desreux, V.; Bisschoff, J. *Bull. Soc. Chim. Belg.* **1950**, *59*, 93.
(21) Broze, G.; Jérôme, R.; Teyssié, Ph.; Gallot, B. *J. Polym. Sci., Polym. Lett. Ed.*, submitted for publication.
(22) Broze, G.; Jérôme, R.; Teyssié, Ph.; Marco, C. *Polym. Bull.*, submitted for publication.

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Molecular Mechanism for $\alpha \rightarrow \delta$ Transformation in Electrically Poled Poly(vinylidene fluoride)

Formation of a polar analogue of the α phase of poly(vinylidene fluoride) (PVF_2) has recently been achieved by Davis et al.,[1] Naegele, Yoon, and Broadhurst,[2] and Davies and Singh.[3] This polar phase (denoted variously as δ, IV, α_p, or II_p) is obtained by conventional or corona poling of thin films of PVF_2 in high electric fields.[1-3] Its

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