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Epimerization of Isotactic Polystyrene

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Summary

A procedure for epimerizing isotactic polystyrene and a Monte-Carlo computer program for simulating polymer epimerization reactions have been developed. The 300 MHz methine proton resonance patterns of partially epimerized isotactic polystyrene and of free radical initiated polystyrene have been analyzed. The latter polymer is essentially atactic (σ=0.45±0.05) and has the same nmr spectrum as completely epimerized polystyrene. Conventional polystyrene therefore seems to be at stereochemical equilibrium.

Introduction

The purpose of this communication is to report a procedure for epimerizing isotactic polystyrene and to describe a Monte-Carlo computer program we have developed for simulating epimerization reactions on polymers. The Monte-Carlo program provides information about n-add stereosequence distributions as a function of reaction time. Results obtained with this program can be used for quantitative interpretations of the pmr and cmr spectra of partially and fully epimerized polymers. We have used this approach in studies on the epimerization of polystyrene and can now interpret the methine proton resonance region quantitatively in terms of triad stereosequence distributions.

Epimerization Procedure

Although the procedure developed by WILLIAMS and FLORY (1969) for epimerizing 2,4-diphenylpentane and 2,4,6-triphenylheptane proved satisfactory for epimerizing conventional polystyrene and poly(3,4,5-trideuteriostyrene) (KINSTLE and HARWOOD 1969, KINSTLE 1970) it was not suitable for the epimerization of isotactic polystyrene. Epimerization was conducted by heating solutions (100mg/5ml) of isotactic polystyrene in carefully

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dried hexamethyl phosphoramide which contained potassium t-butoxide (1M) at 100° for up to 120 hr. The reaction was done under an inert atmosphere to avoid oxidative degradation of the polymer (HOFMANN et al. 1965). Stereochemical equilibrium was obtained after about 14 hr., however. The epimerization products were isolated in nearly quantitative yield by pouring the reaction mixtures into methanol-water mixtures.

PMR Spectra of Epimerized Products

Figure 1 shows the 300 MHz pmr spectra of the epimerization reaction products in tetrachloroethylene solution at 120°. The resonance of methine protons, initially a quintet in the spectrum of isotactic polystyrene, occurs in two general areas in the spectra of most partially epimerized polymers and eventually becomes the same as the pattern observed for free radical initiated polystyrene. This pattern, which is also similar to that described earlier for poly(β,β-dideuteriostyrene) (BROWNSTEIN et al. 1962, SEGRE et al. 1969) consists of a large resonance area at δ=1.65-1.95 ppm and a group of less intense resonances at lower field. The large area has generally been attributed to rr triads by most investigators, who have concluded that free radical initiated polystyrene is predominantly syndiotactic. We show later in this paper that this area must be due to both rr and (rm+mr) triads. This interpretation is consistent with theoretical calculations (FUJIWARA and FLORY 1970, HIRAI et al. 1976, YOON and FLORY 1977), which show that the resonances of methine protons centered in rr and (mr+rm) triads should have chemical shifts that are distinct from the mm-centered proton resonances but which may be fairly close to each other.

Monte-Carlo Simulation of Epimerization

The Monte-Carlo program for simulating polymer epimerization proceeded as follows: Ten-5000 unit cyclic chains were generated in the computer memory. The units were all given initial values of zero, to indicate that they had the same configuration (L-for example). Sites on these chains were selected for "epimerization" by calling numbers from a random number generator. Sites selected were examined for neighboring unit structures (i.e., 1x1 or 1x0 or 0x1 or 0x0, where x is the unit selected). "Epimerization" of the site selected involved calling a second random number (range 0-1) to determine

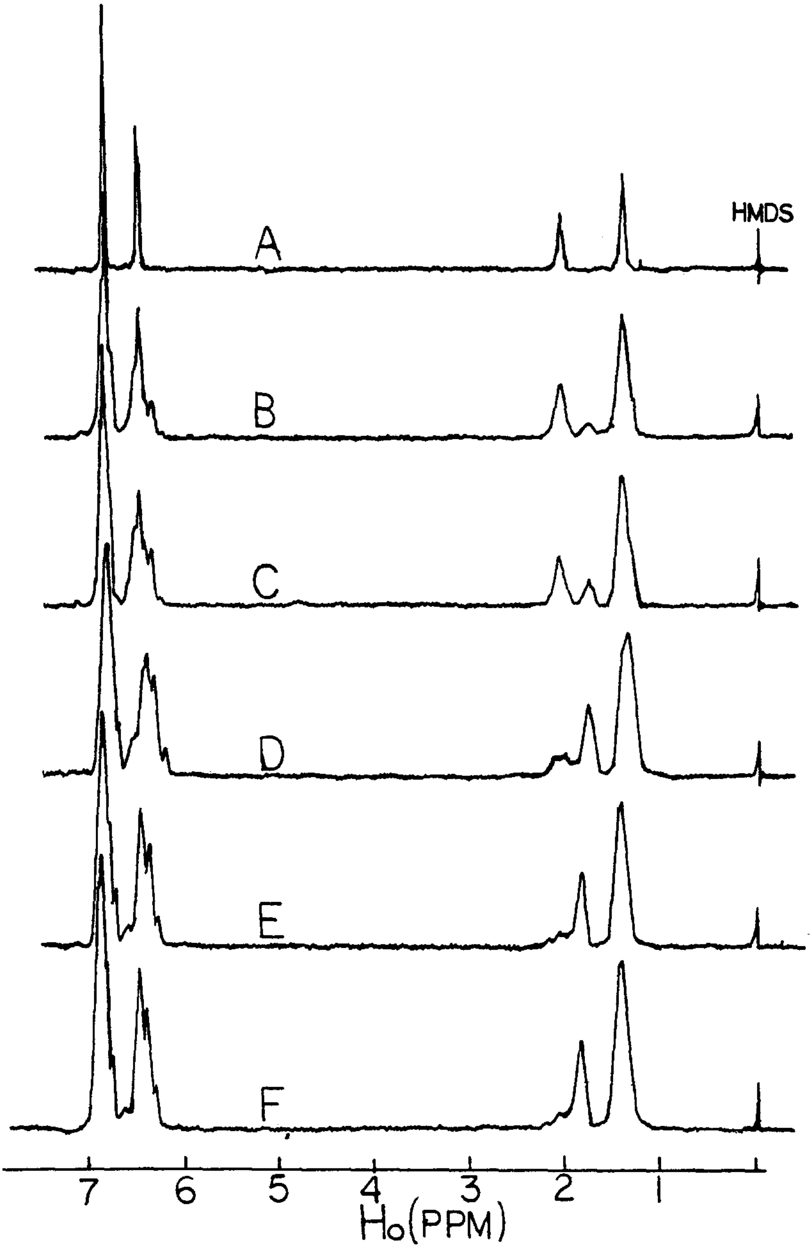

Figure 1. 300 MHz pmr spectra of polystyrenes in C_2Cl_4 solution at 120°. A-Isotactic polystyrene. B, C, D and E-Products of 1.5(B), 2(C), 6(D) and 14(E) hr. epimerizations of isotactic polystyrene. F-Free radical initiated polystyrene.

whether to make the unit selected 1 or 0. When the structure selected had both 1 and 0 neighbors (1x0 or 0x1), the site was given equal probabilities of becoming 1 or 0. When the structure selected had either both 1 or both 0 neighbors (1x1 or 0x0), an assigned probability value (r) was used to define a condition for making the unit selected have the same structure as its neighbors. This condition was met when the second random number selected was greater than or equal to r. The r value used (0.65 was established empirically to be that required to yield the equilibrium distributions of dyads and triads predicted by WILLIAMS and FLORY (1969) for epimerized polystyrene. Each site selection-epimerization step was taken as an arbitrary unit of time. This amounted to assuming that methine protons in all triads were equally accessible to the KOtBu reagent. The site selection-epimerization process was continued until an equilibrium distribution of stereosequences was obtained. The chains were analyzed for dyads, triads, tetrads, pentads and hexads at regular intervals during the calculation and the results obtained were plotted against arbitrary time units to obtain kinetic curves that simulated the epimerization reaction.

Analysis of Methine Proton Resonance Patterns

Figure 2 shows plots of rr and [rr+(mr+rm)] triad distributions as a function of time that were constructed by the method outlined above. Included on the [rr+(mr+rm)] plot are points that represent the proportion of methine proton resonance observed at δ=1.65-195 ppm in the spectra of the partially epimerized polymers. The time scale for these plots was established by placing the datum for the 2 hr. epimerization sample directly on the calculated curve and setting the corresponding abcissa at 2 hr. There is excellent correspondence between these points and the simulated curve. A similar attempt to fit the δ=1.65-1.95 ppm resonance area on the simulated plot of rr versus time was unsuccessful.

These results firmly establish that the resonance observed at δ=1.65-1.95 ppm is due to [rr+(mr+rm)] triads and that the resonances downfield from this area are due to mm triads. Since this latter area is 20-25 percent of the methine proton resonance area in free radical initiated polystyrene, this polymer can be considered to be essentially atactic. Most previously published interpretations of polystyrene spectra which are based on the assumption that polystyrene is primarily syndiotactic (σ=0.3) should be

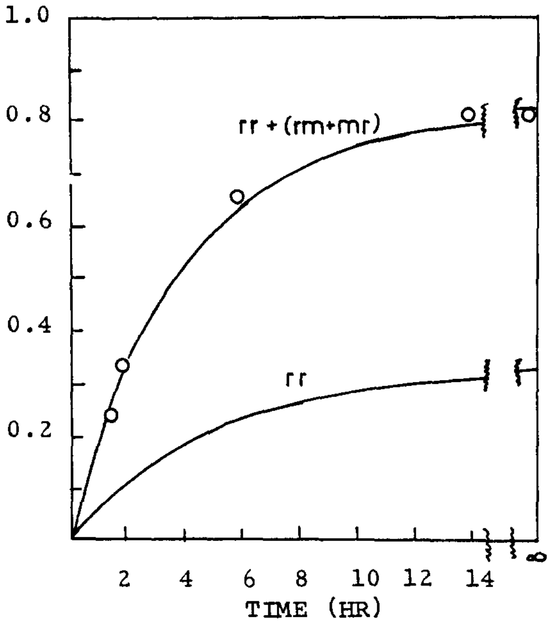

Figure 2: Dyad concentrations in epimerized isotactic polystyrene as a function of reaction time. The data points represent the proportion of methine proton resonance observed at 1.65-1.95 ppm.

reexamined. We are currently investigating the aromatic proton resonances and the methylene and aromatic C-1 carbon resonances of polystyrene, taking advantage of the quantitative information provided by the Monte-Carlo simulation program.

The results shown in Figure 2 provide excellent support for earlier experimental and theoretical work by WILLIAMS and FLORY (1969). Good agreement between experimental and simulated curves would not have been obtained if equilibrium triad distributions predicted by them had been incorrect. In addition, the meso content of free radical initiated polystyrene that is estimated from its methine proton resonance pattern (σ=0.45$\pm$0.05) is in good agreement with recent measurements of the optical anisotropies of polystyrene and poly(p-chlorostyrene) (SUTER and FLORY 1977, SAIZ et al. 1977) which indicate that the meso contents of these polymers are 0.4±0.1.

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