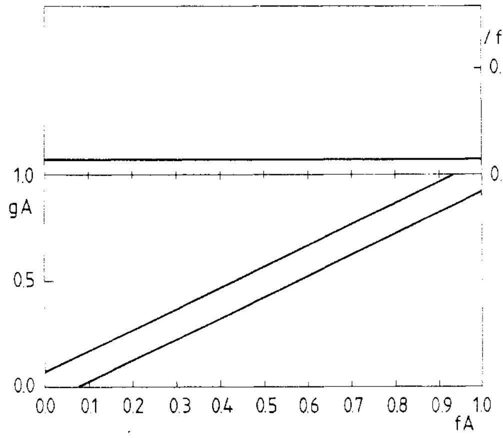

Figure 1. Critical composition difference, $|f_A - g_A|$, is plotted against f_A in the upper region of the figure. The lower region displays g_A versus f_A where the values of g_A are obtained from solving eq 10 for fixed values of the relevant χ's, ϕ_1, N_1, ϕ_2, N_2, θ_1, and θ_2 and f_A. In particular, we examined a 1:1 mixture ($\phi_1 = \phi_2 = 0.5$) of random copolymers ($\theta_1 = \theta_2 = 0.5$) with equal degrees of polymerization ($N_1 = N_2 = 1000$) and $\bar{\chi}_{AB} = 0.3$, $\Delta\chi^a = 1.1$, and $\Delta\chi^b = 0.1$.

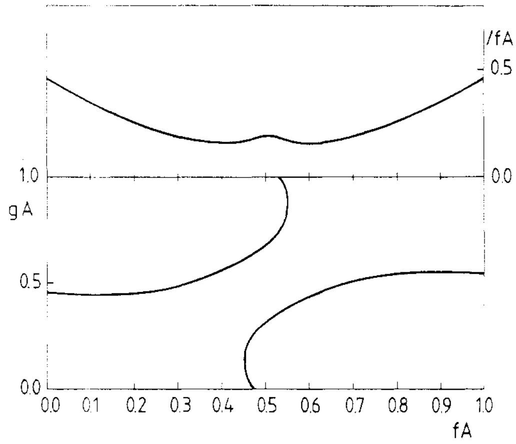

Figure 2. Same as for Figure 1, but with $\bar{\chi}_{AB} = -0.3$, $\Delta\chi^a = 0.5$, and $\Delta\chi^b = 0.7$.

Further work is necessary in order to describe copolymer/copolymer miscibility quantitatively. In particular, we plan to examine eq 10 for various values of the order parameter θ. However, it is now clear that sequence distribution effects may play a major role in determining the miscibility of copolymer mixtures.

Acknowledgment. J.V.H. thanks Eric Beckman for his help in solving of eq 10 via the computer.

References and Notes

(1) Scott, R. L. *J. Polym. Sci.* **1952**, *9*, 423.
(2) Molau, G. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 1007.
(3) Locatelli, J.-L.; Riess, G. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *11*, 257.
(4) Kollinsky, F.; Markert, G. *Makromol. Chem.* **1969**, *121*, 117.
(5) Kollinsky, F.; Markert, G. *Adv. Chem. Ser.* **1971**, *99*, 175.
(6) Koningsveld, R.; Kleintjes, L. A.; Markert, G. *Macromolecules* **1977**, *10*, 1105.
(7) Koningsveld, R.; Kleintjes, L. A. *Macromolecules* **1985**, *18*, 243.
(8) Balazs, A. C.; Sanchez, I. C.; Epstein, I. R. Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1985**, *18*, 2188.
(9) Balazs, A. C.; Karasz, F. E.; MacKnight, W. J.; Ueda, H.; Sanchez, I. C. *Macromolecules* **1985**, *18*, 2784.
(10) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.

Convenient Synthesis of 2,4,6-Trichloroheptane, the Trimer Model of Poly(vinyl chloride)

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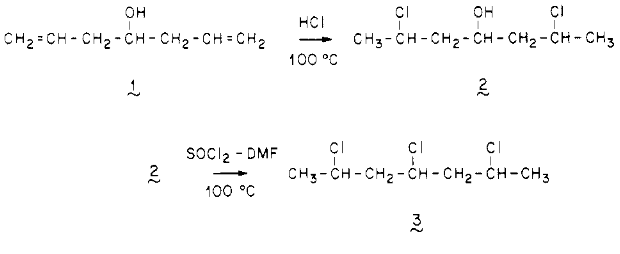
Introduction

For many years 2,4,6-trichloroheptane (**3**) has been employed as a model for poly(vinyl chloride) (PVC) in studies of physical properties. These investigations have included analyses of the vibrational spectra in order to examine the effect of stereochemical structure on conformation,[1-3] stereochemical equilibration to test the theory based on conformational energy calculations,[4-6] interpretations of the NMR spectra based on conformational calculations,[1,7] determinations of molar Kerr constants and dipole moments,[8] the study of transfer reactions involving secondary halogens,[9] and kinetic studies of the tri-*n*-butyltin hydride reductive dechlorination.[10]

The standard synthesis of **3** is a very cumbersome procedure with a yield of <10%.[9] This method involves the hydrogenation of 2,4,6-heptanetrione in the presence of Raney nickel catalyst at a pressure of 140–160 atm. and at 105 °C. The resultant triol is converted to the model trichloride by reaction with thionyl chloride. The combination of the poor yield and the necessity of using a pyrophoric catalyst under vigorous conditions makes this a less than desirable synthetic route.

Some improvements in the above synthesis have been reported. The use of sodium borohydride in the reduction step eliminates the need for high pressures but results in a triol yield of only ~12%.[11] The catalytic hydrogenation of the trione using a nonpyrophoric ruthenium catalyst has also been suggested.[7] In the chlorination of the triol the use of the Vilsmeier reagent, dimethylchloromethyleneammonium chloride, has been found to be more effective than is thionyl chloride.[3] Despite these improvements, the synthesis remains difficult and the yield is unsatisfactory. In order to obtain reasonable quantities of **3** for use in various investigations,[7,8,10] we have developed a new two-step synthetic route using a commercially available starting material, 1,6-heptadien-4-ol (**1**), which results in an acceptable yield of **3**.



$$\underset{1}{CH_2{=}CH{-}CH_2{-}\overset{OH}{\overset{|}{C}H}{-}CH_2{-}CH{=}CH_2} \xrightarrow[100\ ^\circ C]{HCl} \underset{2}{CH_3{-}\overset{Cl}{\overset{|}{C}H}{-}CH_2{-}\overset{OH}{\overset{|}{C}H}{-}CH_2{-}\overset{Cl}{\overset{|}{C}H}{-}CH_3}$$

$$2 \xrightarrow[100\ ^\circ C]{SOCl_2-DMF} \underset{3}{CH_3{-}\overset{Cl}{\overset{|}{C}H}{-}CH_2{-}\overset{Cl}{\overset{|}{C}H}{-}CH_2{-}\overset{Cl}{\overset{|}{C}H}{-}CH_3}$$

Experimental Section

2,6-Dichloro-4-heptanol (2) was prepared by the hydrochlorination of 1,6-heptadien-4-ol (**1**) (Aldrich) with HCl. **1** (0.015 mol) was placed in a 200-mL Wheaton pressure bottle.[12] HCl (0.03 mol) was condensed into the pressure bottle at -98 °C. The rubber seal was closed and the mixture brought to room temperature. The bottle was then placed in an oil bath behind a shield and heated to 100 °C for 20 h with stirring. The pressure within the reaction vessel was calculated to be ~5 atm. After slow cooling to -98 °C to condense residual HCl, the bottle was opened and the dark brown solution poured into a collection flask. The hydrochlorination step was carried out several times due to the limited volume of the reaction vessel but could be scaled up for a larger vessel.

The combined product of several runs was diluted with a 5-fold volume of ether. The solution was then extracted 3 times with

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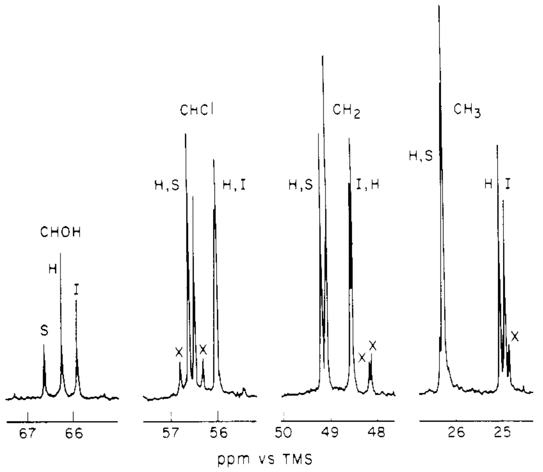

Figure 1. ^{13}C NMR spectrum, 50.31 MHz, of 2,6-dichloro-4-heptanol recorded at 23 °C in acetone-d_6 (X indicates impurity peak).

H_2O, followed by a cautious washing with saturated sodium bicarbonate solution to neutralize the residual HCl. The ether layer was separated and dried over anhydrous sodium sulfate. The ether was removed and the crude material distilled. A fraction of 6-chloro-1-hepten-4-ol (4) was collected (bp 42–47 °C, 0.4 mm). The major fraction isolated was 2 (bp 70–72 °C, 0.4 mm) in a 45% yield. Both intermediates 2 and 4 are apparently new materials and were identified on the basis of their ^{13}C NMR spectra.

2,4,6-Trichloroheptane (3). 2 was converted to 3 by treatment with the complex formed from thionyl chloride and *N*,*N*-dimethylformamide.[13,14] Thionyl chloride (6.4 mL, 0.089 mol) was added dropwise to 32 mL of DMF held at 0 °C with stirring and continuous nitrogen bubbling. (**CAUTION**: This complex has been reported to undergo violent exothermic decomposition upon long standing at room temperature in the presence of traces of metallic impurities;[15] although these conditions are not encountered in this preparation, this reaction should be carried out with appropriate precautions.) 2 (15.0 g, 0.081 mol) was added dropwise over 30 min to the $SOCl_2$–DMF solution held at 0 °C. The resultant mixture was heated to 100 °C for 0.5 h with continuous stirring and nitrogen purging. After cooling to room temperature, 125 mL of H_2O was added. The mixture was extracted 3 times with 75 mL of ether and the combined ether fractions were then washed with water, saturated sodium chloride solution, and finally 5% sodium bicarbonate solution. The ether layer was dried over anhydrous sodium sulfate and the ether was removed. 3 (7.8 g, 0.038 mol) was isolated in 47% yield by distillation (bp 47–49 °C, 0.4 mm (lit. bp 104.5–105.5 °C, 17.0 mm[9])). The overall yield of 3 for this procedure is 21%; however, conditions were not optimized.

^{13}C NMR Measurements. 2, 3, and 4 were examined as 7–50% v/v solutions in acetone-d_6. Hexamethyldisiloxane (HMDS) was used as an internal reference. The proton-decoupled room temperature spectra were recorded at 22.6 and 50.3 MHz on Bruker WH-90 and Varian XL-200 spectrometers, respectively.

Results and Discussion

The two-step synthesis of 1 → 3 provides a convenient and relatively easy method for obtaining useful quantities (5–20 g) of 3. The use of an inexpensive and readily available starting material such as 1 is very desirable. The hydrochlorination follows the Markovnikov rule to give the desired secondary dichloride (2) with a close to random distribution of the stereoisomers. The relative amounts of each of the stereoisomers, isotactic (I), syndiotactic (S), and heterotactic (H), can be measured by comparing the intensities of the carbon resonances as shown in Figure 1. The tentative assignment of resonances to specific stereosequences is based on the strong similarity of the spectrum to that of 3 (see below). The variations in intensities may indicate some preference for the isotactic isomer, but we have not confirmed the chemical shift assignments by the isolation of the isomers of 2. The monochlorinated alcohol (4) was also isolated and is identified by the unique stereochemical doublets at 53.6 (CHCl), 114.9 ($=CH_2$), and 120.8 ppm ($=CH$). The NMR indicates no unreacted starting material after the hydrochlorination step.

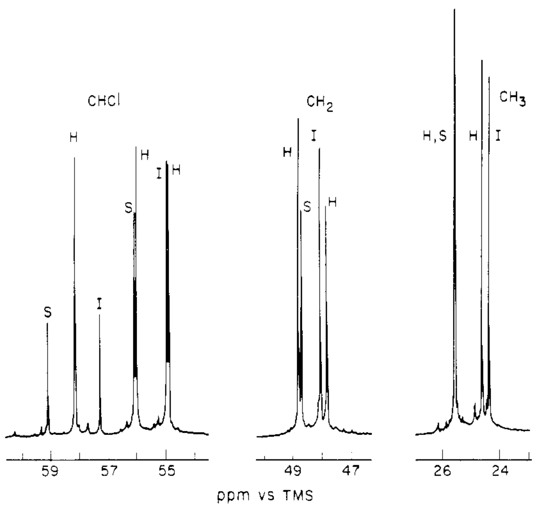

Figure 2. ^{13}C NMR spectrum, 50.31 MHz, of 2,4,6-trichloroheptane recorded at 23 °C in acetone-d_6.

The conversion of the secondary alcohol, 2, to the trichloride, 3, is accomplished with the use of thionyl chloride complexed with *N*,*N*-dimethylformamide. This procedure eliminates the rearrangement which may occur with the use of thionyl chloride alone and is thought to proceed via formation of the alkoxyformamidinium intermediate $[Me_2N^+{=}CHOR]X^-$.[13] The ^{13}C NMR spectrum of the final product of this synthesis is shown in Figure 2. The assignment of the resonances has been previously established.[7] Since the conversion of the alcohol to the chloride is expected to occur with complete inversion of configuration,[13] the random stereochemistry of the chlorination step should be maintained in the trichloride. This result is confirmed by the relative sizes of the resonances which indicate a random distribution of stereochemical isomers in 3. Each of the seven carbons in the heterotactic isomer of 3 will produce a single resonance. Because of symmetry the syndiotactic and isotactic isomers will each produce four resonances in a 2:2:2:1 ratio with the central CHCl (~58 ppm) having the count of one. Since there are two ways to form the heterotactic isomer, the amount of this isomer will be equal to the sum of the amounts of isotactic and synditactic isomers in a random distribution. Therefore, all of the resonances should be of similar intensity except for the central CHCl of the syndiotactic and isotactic isomers. On the basis of the NMR results, product 3 is estimated to be about 90% pure. The trichloride can be further purified and the individual stereoisomers can be separated by gas chromatography according to the method established by Flory and Pickles.[5] Using this GC method we have succeeded in isolating each stereoisomer with an isomeric purity greater than 90%.[7]

In summary, we have developed a convenient synthesis of the stereoisomers of trichloroheptane. The starting material is inexpensive and readily available. The method avoids most of the complications of previous procedures and improves the yield of the product. Therefore, the mixture of trichloroheptane stereoisomers and the individual isomers separated by GC are made readily available for use as the model trimers in studies of the physical properties of PVC.

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Registry No. **1**, 2883-45-6; **2**, 113569-09-8; **3**, 13049-21-3; **4**, 113569-10-1; PVC, 9002-86-2.

References and Notes

(1) Doskocilovâ, D.; Stokr, J.; Schneider, B.; Pivcovâ, H.; Kolinský, M.; Petrânek, J.; Lim, D. *J. Polym. Sci., Part C* **1967**, *16*, 215.
(2) Moore, W. H.; Krimm, S. *J. Mol. Spectrosc.* **1974**, *51*, 1.
(3) George, W. O.; Goodfield, J. E.; Maddams, W. F. *Spectrochim. Acta, Part A* **1985**, *41A*, 1243.
(4) Flory, P. J.; Williams, A. D. *J. Am. Chem. Soc.* **1969**, *91*, 3118.
(5) Flory, P. J.; Pickles, C. J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 632.
(6) Boyd, R. H.; Kesner, L. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 375.
(7) Tonelli, A. E.; Schilling, F. C.; Starnes, W. H., Jr.; Shepherd, L.; Plitz, I. M. *Macromolecules* **1979**, *12*, 78.
(8) Khanarian, G.; Schilling, F. C.; Cais, R. E.; Tonelli, A. E. *Macromolecules* **1983**, *16*, 287.
(9) Lim, D.; Kolinský, M. *J. Polym. Sci.* **1961**, *53*, 173.
(10) Jameison, F. A.; Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1986**, *19*, 2168.
(11) Dale, J. *J. Chem. Soc.* **1961**, 910.
(12) The Wheaton pressure bottle can be purchased from American Scientific Products; a Teflon-lined, stainless steel pressure bomb may be substituted if available.
(13) Hudson, H. R.; de Spinoza, G. R. *J. Chem. Soc., Perkins Trans. 1* **1976**, 104.
(14) Starnes, W. H., Jr.; Plitz, I. M.; Hische, D. C.; Freed, D. J.; Schilling, F. C.; Schilling, M. L. *Macromolecules* **1978**, *11*, 373.
(15) Spitulnik, M. J. *Chem. Eng. News* **1977**, *55*, 31.

Effect of Complexing Agents on the Rate of Polymerization in Systems Involving Dormant Aggregated Polymers and Living Nonaggregated Polymers

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Lithium salts of polystyrene or polydienes are aggregated in hydrocarbon solvents. The aggregates are inert and the polymerization is carried out by a minute amount of unassociated polymers which are in equilibrium with the aggregates. Various solvating agents may dissociate the aggregates by being complexed with the unassociated polymers. The resulting complexes have usually a 1:1 stoichiometry and contribute to propagation; however, their rate of growth is, on the whole, different from that of the unassociated polymers.

Let us consider polymerization of lithium polystyrene, denoted here by P*, in a hydrocarbon solvent. In such solvents the polymers form dimeric aggregates $P*_2$ which are in equilibrium with P*, i.e.,

$$P*_2 \rightleftarrows 2P* \qquad K_{diss}$$

while

$$P*_{n\text{-mer}} + M \rightarrow P*_{(n+1)\text{-mer}} k_p$$

with M denoting the monomer. In the presence of a complexing agent denoted by C an additional equilibrium is assumed to be established: namely,

$$P* + C \rightleftarrows (P*,C) \qquad K_c$$

yielding a 1:1 complex propagating with a rate constant k_c. The observed rate of propagation, R, per monomer, should be given therefore by

$$R = -d \ln [M]/dt = k_p[P*] + k_c[(P*,C)] \qquad (1)$$

Obviously, R increases with increasing C for $k_c > k_p$, but the dependence on C is more complex when $k_c < k_p$. It is our intention to examine such a dependence and to derive an expression giving R as a function of [C] and of X—the total concentration of the polymers in whatever form.

From the following balanced equation

$$2[P*]^2/K_{diss} + [P*] + K_c[C][P*] = X \qquad (2)$$

one finds, for a constant X, the derivative

$$d[P*]/d[C] = -K_c[P*]/(1 + 4[P*]/K_{diss} + K_c[C]) \qquad (3)$$

to be negative demonstrating, as expected, that [P*] decreases with increasing [C]. In view of eq 1, one gets for a constant X

$$dR/d[C] = K_c[P*][k_c - (k_p + k_cK_c[C])/(1 + K_c[C] + 4[P*]/K_{diss})]$$

and hence the initial slope of R plotted as a function of [C] is

$$(dR/d[C])_{[C]=0} = K_c[P*][k_c - k_p/(1 + 4[P*]/K_{diss})]$$

i.e., the rate of polymerization increases with [C] when

$$(k_c/k_p)(1 + 4[P*]/K_{diss}) > 1$$

and decreases when

$$(k_c/k_p)(1 + 4[P*]/K_{diss}) < 1$$

Note, these inequalities are independent of the value of [C] since they refer to the effect caused by the addition of very small amounts of the complexing agent.

For most of the studied systems $[P*] \ll X$ and then the approximation $[P*] \sim (^1/_2K_{diss}X)^{1/2}$ is justified when the concentration of the complexing agent is low. Under such conditions the rate of polymerization decreases on addition of small amounts of C when

$$(k_c/k_p)[1 + (4/2^{1/2})X^{1/2}/K_{diss}{}^{1/2}] < 1$$

or, since $(4/2^{1/2})X^{1/2}/K_{diss}{}^{1/2} \gg 1$ under conditions prevailing in polymerization, the rate of propagation decreases when

$$X < (k_p/k_c)^2K_{diss}/8$$

provided that $k_c < k_p$.

In conclusion, initial addition of a complexing agent to a dimerically aggregated lithium polystyrene, or to another similarly aggregated living polymer, increases the rate of polymerization when the total concentration of polymers, in all its forms, exceeds $(k_p/k_c)^2K_{diss}/8$ and decreases it when the inequality is reversed, provided that $k_c < k_p$.

The results reported by Hélary and Fontanille[1,2] provide an illustration of the above principle. Coordination of lithium polystyrene with tetramethylethylenediamine in cyclohexane increases the rate of propagation for X = 8.3 mM and decreases it when X = 0.93 mM. Their studies led to $k_c = 0.15\ M^{-1}\ s^{-1}$ at 25 °C, hence the constant $k_p(K_{diss}/2)^{1/2}$ could be calculated on the basis of our treat-

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