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Steric Effect of Acyl Substituent on Homopolymerization of 7,8-Diacyl-7,8-dicyanoquinodimethanes

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ABSTRACT: Quinodimethane compounds with different substituents such as cyano and acyl groups at the 7 and 8 positions are obtainable as stable crystals and are homopolymerizable with anionic and radical initiators. Their homopolymerizations were found to exhibit a typical equilibrium polymerization behavior, the kinetics analysis of which allowed determination of their thermodynamic parameters of polymerization. Their values were compared with the substituent parameters of the acyl groups by means of linear free energy relationships, which showed that their enthalpy of polymerization is predominantly related with the Taft E_s values of the acyl groups and independent of σ^* values ($\rho = 0$), indicating that their homopolymerizability is determined exclusively by a steric effect of the acyl groups.

Introduction

Unsubstituted 1,4-benzoquinodimethane is so reactive that, when it is prepared, it polymerizes spontaneously to give the polymer and the dimers.[1] When electron-accepting substituents are fully introduced at the 7 and 8 positions, compounds such as 7,7,8,8-tetracyanoquinodimethane (TCNQ)[2] and 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane[3] form stable crystals at room temperature that do not homopolymerize. On the other hand, it was found that quinodimethanes with two different substituents at the 7 and 8 positions, for instance, 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane,[4–6] 7,8-diacyl-7,8-dicyanoquinodimethane,[7] and 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane,[8] not only are obtainable as stable crystalline compounds but also are homopolymerizable with various types of initiators. Moreover, their polymerization kinetics interestingly revealed that their homopolymerization with radical initiators was a typical equilibrium polymerization involving considerable depolymerization.[9] The entropy change during their polymerization was in the range 35–40 J/(K·mol), which was about one-third as large as that of the corresponding conventional vinyl compounds. The enthalpy change of polymerization was also small and varied with the substituents. Thus, combination of the two values results in a negative free energy value of polymerization for these compounds, which is small near room temperature. If we prepare several equilibrium-polymerizable 7,8-diacyl-7,8-dicyanoquinodimethanes with different acyl groups, kinetics studies of their polymerizations will permit us to obtain precise values for their thermodynamic parameters of polymerization without great difficulty. We can then correlate these values with the acyl substituents by means of a linear free energy relationship to look into the nature of the polymerizability of the compounds. To date, such a relationship has not been extensively investigated, because only a limited number of equilibrium-polymerizable monomers are currently available.

In this work, some new derivatives of 7,8-diacyl-7,8-dicyanoquinodimethane (**3**), namely, 7,8-bis(phenylacetyl)- (**3a**), 7,8-dipropionyl- (**3b**), and 7,8-diisobutyryl-7,8-dicyanoquinodimethane (**3c**), were prepared, and the kinetics of their radical polymerization was studied to obtain their thermodynamic parameters of polymerization. These were analyzed together with the corresponding data[9] for 7,8-dibenzoyl- (BzCQ) and 7,8-diacetyl-7,8-dicyanoquinodimethane (AcCQ), which have been reported previously, by means of a linear free energy relationship (Taft's equation).

Experimental Section

Preparation of 7,8-Diacyl-7,8-dicyano-*p*-xylene (2). Sodium ethoxide (3.26 g, 48 mmol) was dissolved in 80 mL of dry *p*-dioxane, and 3.0 g (19.2 mmol) of 7,8-dicyano-*p*-xylene (**1**) and the appropriate ethyl ester (44 mmol), i.e., 7.22 g of ethyl phenylacetate for 7,8-bis(phenylacetyl)-7,8-dicyano-*p*-xylene (**2a**), 4.50 g of ethyl propionate for 7,8-dipropionyl-7,8-dicyano-*p*-xylene

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Scheme I

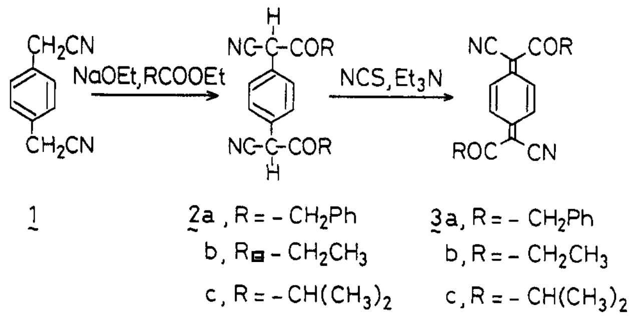


Table I
First Reduction Potentials[a]

compd	E_1/V[b]	compd	E_1/V[b]
3c	-0.10	**3b**	+0.01
3a	-0.05	AcCQ	+0.03
BzCQ	-0.02	TCNQ	+0.19

[a] Solvent, dichloromethane containing tetrabutylammonium perchlorate (0.1 mol/L); reference electrode, Ag/AgCl. [b] Relative error, ±0.01 V. Scan rate, 100 mV/s.

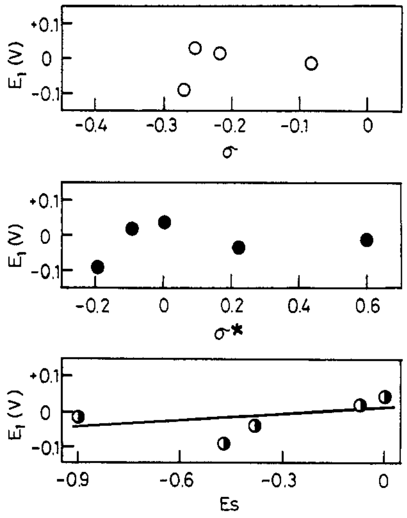


Figure 1. Plots of E_1 versus σ (○), σ^* (●), and E_s (◐) for **3a**, **3b**, **3c**, AcCQ, and BzCQ.

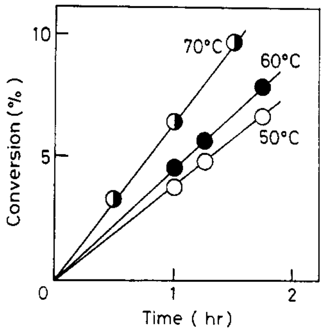


Figure 2. Time–conversion curves for the polymerization of **3a** at various temperatures: 50 (○), 60 (●), and 70 (◐) °C. [**3a**] = 1.01×10^{-2} mol/L; [AIBN] = 1.38×10^{-4} mol/L.

(**2b**), and 5.12 g of ethyl isobutyrate for 7,8-diisobutyryl-7,8-dicyano-*p*-xylene (**2c**), were added to the solution. After it was refluxed under nitrogen for 3 h, the reaction mixture was placed under reduced pressure to remove volatile materials. A dark brown solid was obtained, to which water was added to dissolve it. Dilute hydrochloric acid was added until the mixture became acidic. A yellow solid precipitated, which was filtered and dried under reduced pressure to obtain crude **2**. This solid was recrystallized from acetonitrile for **2a** and from isopropyl ether for **2b** and **2c**.

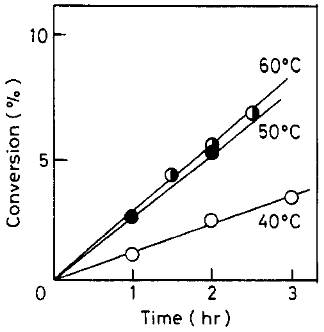


Figure 3. Time–conversion curves for the polymerization of **3b** at various temperatures: 40 (○), 50 (●), and 60 (◐) °C. [**3b**] = 1.71×10^{-2} mol/L; [AIBN] = 1.38×10^{-4} mol/L.

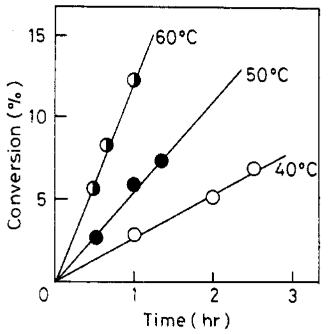


Figure 4. Time–conversion curves for the polymerization of **3c** at various temperatures: 40 (○), 50 (●), and 60 (◐) °C. [**3c**] = 3.50×10^{-2} mol/L; [AIBN] = 1.38×10^{-4} mol/L.

2a: yield 55.1%; mp 135–136 °C; IR (KBr) $\nu_{C\equiv N}$ 2220, $\nu_{C=O}$ 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.33 (s, 4 H), 4.77 (s, 22 H), 3.88 (s, 4 H). Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14. Found: C, 79.32; H, 5.21; N, 7.18.

2b: yield 43.1%; mp 195–196 °C; IR (KBr) $\nu_{C\equiv N}$ 2220, $\nu_{C=O}$ 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.48 (s, 4 H), 4.68 (s, 2 H), 2.63 (q, J = 6.6 Hz, 4 H), 1.06 (t, J = 6.6 Hz, 6 H). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.54; H, 5.98; N, 10.49.

2c: yield 62.4%; mp 139–140 °C; IR (KBr) $\nu_{C\equiv N}$ 2190, $\nu_{C=O}$ 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.42 (s, 4 H), 4.82 (s, 2 H), 2.92 (m, 2 H), 1.06 (d, J = 6.6 Hz, 12 H). Anal. Calcd for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45. Found: C, 72.77; H, 6.74; N, 9.48.

Preparation of 3a. Compound **2a** (0.7 g, 1.78 mmol) was suspended in 5 mL of acetonitrile under nitrogen. To the suspension kept at 0 °C was added 0.47 g (3.52 mmol) of *N*-chlorosuccinimide (NCS). After the mixture was stirred for 3 min, a few drops of triethylamine were added until its color changed from yellow to orange. The orange solid was filtered off and dried under reduced pressure. The solid was dissolved in 80 mL of dichloromethane, and the insoluble portion, unreacted **2a**, was removed by filtration. The filtrate was evaporated under reduced pressure to obtain an orange solid, which was recrystallized from dichloromethane to give crystalline orange plates of **3a**.

3a: yield 11.4%; mp 185 °C dec; IR (KBr) $\nu_{C\equiv N}$ 2200, $\nu_{C=O}$ 1690, $\nu_{C=C}$ 1540 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.23 (dd, J = 10.8 Hz, J = 1.8 Hz, 2 H), 7.39 (dd, J = 10.8 Hz, J = 1.8 Hz, 2 H), 7.31 (s, 10 H), 4.20 (s, 4 H); UV-vis (CHCl$_3$) λ_{max} = 420 nm (ϵ = 4.26×10^4). Anal. Calcd for $C_{26}H_{18}N_2O_2$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.95; H, 4.58; N, 7.20.

Preparation of 3b and 3c. Compound **2b** (0.6 g, 2.24 mmol) or **2c** (0.6 g, 2.02 mmol) was suspended in 100 mL of chloroform under nitrogen. To the suspension kept at 0 °C was added 0.47 g (3.52 mmol) of NCS. After 5 min of stirring, a few (2–3) drops of triethylamine were added to change the yellow suspension to a red homogeneous solution, which was washed twice with ice water (100 mL × 2) and 50 mL of 2% sodium bicarbonate aqueous solution and dried over anhydrous magnesium sulfate. The solution was evaporated under reduced pressure to remove chloroform. The remaining red solid was recrystallized from a toluene–hexane mixture to give crystalline orange

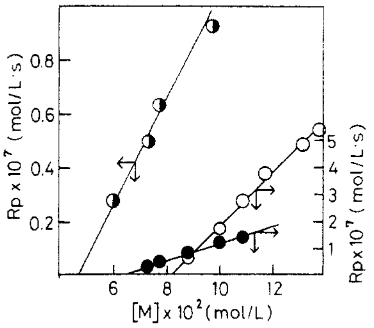


Figure 5. Plots of R_p versus [M] for the polymerization of **3a** at various temperatures: 50 (◑), 60 (●), and 70 (○) °C. [AIBN] = 1.38×10^{-2} mol/L.

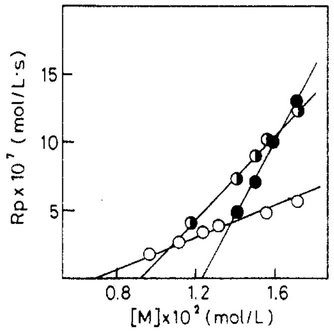


Figure 6. Plots of R_p versus [M] for the polymerization of **3b** at various temperatures: 40 (○), 50 (◑), and 60 (●) °C. [AIBN] = 1.38×10^{-4} mol/L.

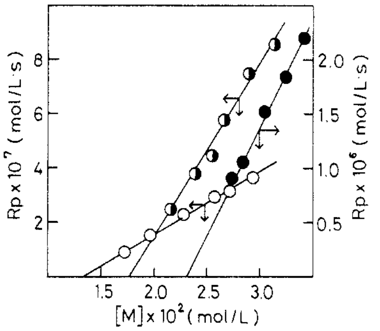


Figure 7. Plots of R_p versus [M] for the polymerization of **3c** at various temperatures: 40 (○), 50 (◑), and 60 (●) °C. [AIBN] = 1.38×10^{-4} mol/L.

Table II
Equilibrium Monomer Concentration, $[M]_e$, for the Polymerizations of 3a, 3b, 3c, AcCQ, and BzCQ

		$[M]_e \times 10^3$, mol/L				
T, °C	$1/T \times 10^3$	3a	3b	3c	AcCQ	BzCQ
40	3.19		7.05	13.2	4.98	23.6
50	3.10	4.8	9.4	17.5	6.51	29.5
60	3.00	6.4	12.4	22.7	9.17	36.6
70	2.92	8.2			11.2	47.9

plates of **3b** or **3c**.

3b: yield 5.0%; mp 210 °C; IR (KBr) $\nu_{C\equiv N}$ 2200, $\nu_{C=O}$ 1690, $\nu_{C=C}$ 1530 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.35 (dd, J = 10.2 Hz, J = 1.8 Hz, 2 H), 7.43 (dd, J = 10.2 Hz, J = 1.8 Hz, 2 H), 2.99 (q, J = 6.6 Hz, 4 H), 1.19 (t, J = 6.6 Hz, 6 H); UV-vis (CHCl$_3$) λ_{max} = 412 nm (ϵ = 4.18×10^4). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.17; H, 5.30; N, 10.52. Found: C, 72.12; H, 5.24; N, 10.58.

3c: yield 11.8%; mp 220 °C dec; IR (KBr) $\nu_{C\equiv N}$ 2200, $\nu_{C=O}$ 1690, $\nu_{C=C}$ 1530 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.21 (dd, J = 9.6 Hz, J = 1.8 Hz, 2 H), 7.43 (dd, J = 9.6 Hz, J = 1.8 Hz, 2 H), 3.39 (m, 2 H), 1.22 (d, J = 6.6 Hz, 12 H); UV-vis (CHCl$_3$) λ_{max} = 411 nm (ϵ = 3.89×10^4). Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.44; H, 6.18; N, 9.52. Found: C, 73.34; H, 6.11; N, 9.60.

Homopolymerization Kinetics. Given amounts of the monomer 3, 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator, and two drops of acetic acid as an anionic polymerization inhibitor were dissolved in chloroform in a 10-mL volumetric flask to prepare a monomer solution of known concentration. A 5-mL aliquot (for monomers **3a** and **3b**) or 2-mL aliquot (for monomer **3c**) was pipetted into an ampule, which was degassed completely by the freeze–thaw method (repeated twice) and sealed. The ampule was set in a thermostated bath at 40, 50, 60, or 70 °C for the time of polymerization and then opened. The concentration of the monomer was determined spectrophotometrically using the absorption bands of 420, 412, and 411 nm, which are characteristic for **3a**, **3b**, and **3c**, respectively. The polymerization rate, R_p, was calculated from the amounts of monomer consumed as a function of time.

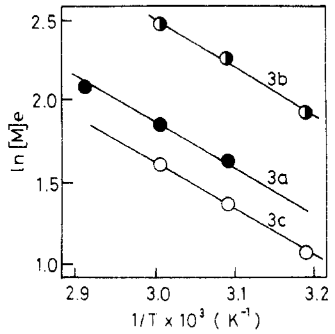
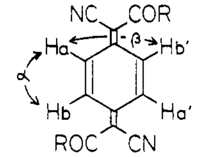


Figure 8. Plots of ln $[M]_e$ versus $1/T_c$ for the polymerizations of **3a** (●), **3b** (◑), and **3c** (○).

Characterization. The first reduction potentials of **3a–c** were determined by voltammetric measurement using dichloromethane with tetrabutylammonium perchlorate (0.1 mol/L) as solvent and a Ag/AgCl electrode, a glassy carbon electrode, and a platinum wire as reference, working, and third electrodes, respectively.

Results and Discussion

The NMR spectra of **3a–c** exhibit two double doublets at 8 and 7 ppm due to the protons on the quinodimethane nucleus. The coupling constants of 10.8–9.6 and 1.8 Hz are in good agreement with the α-coupling (6–10 Hz) of H_a with H_b and the β-coupling (1–3 Hz) of H_a with $H_{b'}$ on the nucleus of the anti form of compounds 3.



Therefore, we concluded that **3a–c** exist as the anti isomer. Values of the first reduction potential, E_1, of **3a–c** measured by cyclic voltammetry are listed in Table I, together with those of TCNQ, BzCQ, and AcCQ. Within the limited range of the compounds under consideration, the values of E_1 did not correlate well with the σ and σ^* values of the R substituents of the acyl groups (RCO). A better, but somewhat ambiguous, correlation is obtained with the bulkiness index of the substituents, such as Taft's steric effect parameter, E_s, as shown in Figure 1. The number of compounds available for study is so small that a definite conclusion cannot be reached at this time.

Kinetics of Polymerization. The relationships of the polymer yield versus time, so-called time–conversion curves, for the homopolymerizations of **3a** at 50, 60, and 70 °C, of **3b** at 40, 50, and 60 °C, and of **3c** at 40, 50, and 60 °C are shown in Figures 2–4, respectively. In all runs the polymerizations took place without an induction period. At low conversions, the polymer yields increase linearly

Table III
Enthalpy Changes (ΔH), Entropy Changes (ΔS), and Substituent Constants for the Polymerizations of 3a, 3b, 3c, AcCQ, and BzCQ

monomer	R	σ^b	σ^{*b}	$E_s{}^b$	ΔH, kJ/mol	$\Delta\Delta H$	$\Delta\Delta H - 4E_s$	ΔS, J/(K·mol)
3a	benzyl		+0.215	−0.38	24.6	−0.8	0.7	37.0
3b	ethyl	−0.218	−0.10	−0.07	24.5	−0.7	−0.42	37.0
3c	isopropyl	−0.276	−0.19	−0.47	23.5	−1.9	0	39.1
AcCQ[a]	methyl	−0.256	0.00	0.00	25.4	0	0	36.9
BzCQ[a]	phenyl	−0.085	0.60	−0.90	21.6	−3.8	−0.2	36.9

[a] Values from ref 9. [b] Values from ref 12.

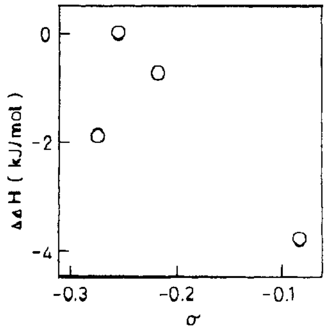


Figure 9. Hammett plot of $\Delta\Delta H$ versus σ for the homopolymerizations of **3b**, **3c**, AcCQ, and BzCQ.

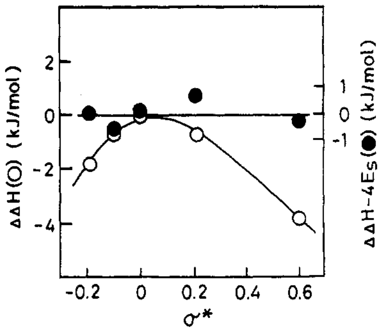


Figure 10. Hammett plot of $\Delta\Delta H$ versus σ^* (○) and Taft plot of $\Delta\Delta H - 4E_s$ versus σ^* (●) for the homopolymerizations of **3a**, **3b**, **3c**, AcCQ, and BzCQ.

with the time of polymerization; the slope of the straight line gives the rate of polymerization, R_p. According to the method of Vofsi and Tobolsky,[10] the rates of polymerization were plotted versus monomer concentration, [M], at various temperatures as shown in Figures 5–7 for **3a**, **3b**, and **3c**, respectively. The extrapolation of the linear relationship of R_p versus [M] to a zero rate allowed us to determine the values of equilibrium monomer concentration $[M]_e$, at the different polymerization temperatures. The $[M]_e$ values are summarized in Table II. The relationship between equilibrium monomer concentration, $[M]_e$, and reciprocal of ceiling temperature, $1/T_c$, is shown in Figure 8. The linear relationship is expressed by the equation[11]

$$\ln [M]_e = \Delta H/RT_c - \Delta S/R \qquad (1)$$

where ΔH and ΔS are enthalpy and entropy changes for polymerization between the monomer and the polymer, respectively, and R is the gas constant. The values for the enthalpy change (ΔH) and the entropy change (ΔS) for the polymerizations of **3a–c** are summarized in Table III, together with the data for AcCQ and BzCQ.

The entropy change (ΔS) for the polymerizations of **3a**, **3b**, **3c**, AcCQ, and BzCQ is almost constant and one-third as large as the corresponding value for vinyl and related compounds. This is conceivably one important general feature of homopolymerizable quinodimethanes.

The enthalpy changes (ΔH) were examined in linear free energy relationships such as the Hammett and Taft equations[12]

$$\Delta H = \rho\sigma \qquad (2)$$

and

$$\Delta H = \rho^*\sigma^* + SE_s \qquad (3)$$

where σ is a constant characteristic of the substituent, generally referred to as Hammett's substituent constant, ρ is a constant for the particular reaction, σ^* is a polar substituent parameter, ρ^* is a measure of sensitivity to polar effect, E_s is a steric effect parameter of a substituent, and S is a measure of sensitivity of steric effect. Also in the Table III are listed values of σ, σ^*, and E_s for the R groups of the acyl (RCO) substituents at the 7 or 8 position of the substituted quinodimethanes. As shown in Figure 9, ΔH are not found to be correlated with σ. As shown in Figure 10, the Hammett plot (○) between ΔH and σ^* is found to be convex. If the steric hindrance is taken into account by subtracting $4E_s$ from ΔH, the plot (●) becomes a straight line with zero slope; i.e., $\rho^* = 0$. It is obvious therefore that the enthalpy change of polymerization is dependent only on the steric hindrance of the substituents and, interestingly, is not influenced any more by the polar effect of the substituents. We can conclude, at least within the limited range of equilibrium-polymerizable quinodimethane monomers with different substituents, cyano and acyl groups, at the 7 and 8 positions, that their polymerizability is exclusively determined by the steric hindrance of the acyl groups. This conclusion is reminiscent of the steric effect of alkylthio groups on the polymerization behavior of captodatively substituted quinodimethanes; 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane can easily be polymerized with free radical, cationic, and anionic initiators, while 7,8-bis(*tert*-butylthio)-7,8-dicyanoquinodimethane does not polymerize with any initiator.[8] Furthermore, there are many suggestions about the influence of the steric hindrance of substituent on ring-opening polymerizations: cycloalkanes,[13] methyl- and ethylcyclobutane are polymerizable, while isopropylcyclobutane does not polymerize; lactams[14,15] pyrrolidone and 5-ethyl-, 5-*n*-propyl-, 5-*tert*-butyl-, and 5-cyclohexyl-ε-caprolactam are polymerizable, while 1-methyl- and 5-(ethoxycarbonyl)pyrrolidone and 5-*n*-heptyl- and 5-phenyl-ε-caprolactam do not polymerize; lactones,[16] δ-valerolactone is polymerizable, while 2-*n*-propyl- and 5-methyl-δ-valerolactone do not polymerize; ethers,[17] tetrahydrofuran is polymerizable, while 2-methyl-, 2-(chloromethyl)-, and 3-methyltetrahydrofuran do not polymerize. Surely, introduction of a bulky substituent into a monomer eliminates its ability to polymerize.[11] As to alkyl methacrylates, ester residues such as methyl, ethyl, and *n*-butyl do not significantly affect the enthalpy of polymerization, but bulky residues such as *tert*-butyl, cyclohexyl, and phenyl do lower it slightly.[18] The steric hindrance effect on polymerization of monomers has already been accepted in a qualitative sense,[11] but a quantitative confirmation has not been found yet owing to the difficulty of obtaining accurate values for the thermodynamic parameters of polymerization for a homologous series of monomers. However, this paper appears to present the first confirmation of a steric effect of the monomer substituents on the polymerization in a quantitative sense. The present conclusion is surely not applicable yet to the polymerizations of a wide range of monomers.

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Solvent Dependence of the Chain Dimensions of Poly[illegible]xyl isocyanate)

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ABSTRACT: Poly(*n*-hexyl isocyanate), known to be a stiff helical polymer, is found experimentally to have persistence lengths of from 20 to 40 nm, depending upon the solvent in which the measurements are made. The origin of this solvent dependence is hypothesized in the present work to be due to a local interaction of polar solvents with the chain backbone, giving rise to greater torsional oscillations around the backbone bonds. NMR line-width measurements made on the same sample of polymer in a variety of solvents support this idea by showing that the magnitude of the polymer's local motion is correlated with solvent polarity.

Introduction

Poly(*n*-alkyl isocyanates)[1–7] have been known for some time to be stiff rod-like macromolecules, particularly when viewed on a short length scale.[2–7] It is generally accepted that the rod-like structure is a result of a helical twist to the chain, which arises from a competition between electronic and steric factors.[6,7] The structure of the crystalline state also reflects this feature, exhibiting a repeat unit involving eight monomers per three turns.[8] These polymers represent important experimental systems with which to test theories of wormlike chains[9–11] and theories for the formation of liquid crystals.[12] Thus their solution properties have been studied extensively by light scattering and hydrodynamic methods.[4–6,9,13,14] As expected, the molecular rods are not perfectly stiff in solution. This has been demonstrated experimentally by measurements sensitive to the overall chain dimensions, which show a gradual transition from rod-like to coil-like behavior with increasing molecular weight.[4,7,11]

An unusual solvent dependence of the global dimensions of poly(*n*-hexyl isocyanate) that suggests a general decrease in polymer dimension with increasing polarity of the solvent was first uncovered by Schneider et al.[2] and later investigated in greater depth by Berger and Tidswell.[6] This dependence is illustrated in Table I, where the Berger and Tidswell data for the intrinsic viscosity, $[\eta]$, of a $M_w = 2.04 \times 10^5$ fraction are displayed for a variety of solvents whose viscosities, η_{solv}, and dipole moments, μ_{solv}, are also given. The general decrease of $[\eta]$ with increasing solvent polarity is a result of smaller

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