

Synthesis of Multicyano-substituted Cyclopropylphenyl Vinyl Carbonates and Their Polymerization Behaviors

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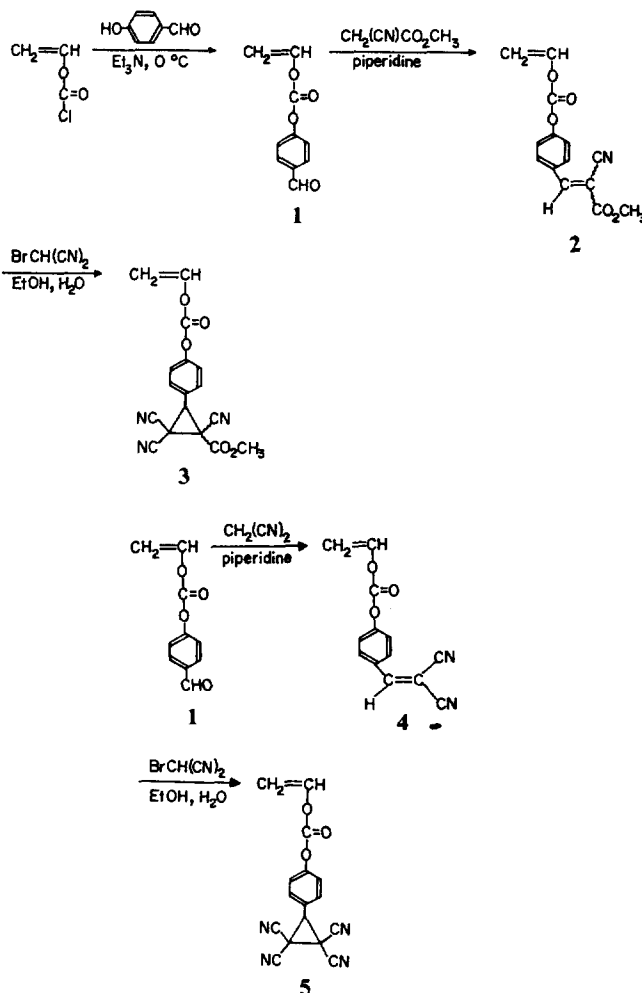
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Piezoelectric polymers have long been the subject of curiosity and have caused recent interest.¹ It is well-known that crystalline polymers having large dipole moment can exhibit piezoelectric effects if the main chains have all-planar zigzag structure. The best known polymer is crystalline poly(vinylidene fluoride).² Amorphous polymers with a high concentration of dipole moments can also show piezoelectric properties after poling, such as the copolymer of vinylidene cyanide and vinyl acetate.³ Poly(acrylonitrile) has high concentrations of nitrile dipoles, but the helical structure of the polymer chains causes the radiating dipoles to cancel each other.⁴ In the case of poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation resulting in high piezoelectric activity.⁵

A potentially piezoelectric polymer must contain a large concentration of dipoles and be able to withstand high voltages without breakdown. The polymers have to be film-forming and mechanically very strong. We have recently proposed that three- and four-membered rings with multi-cyano substituents held rigidly in alignment will have large dipole moments and these polymers are potentially piezoelectric materials.⁶ We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane,⁶⁻⁸ 1,1,2-tricyano-2-carbomethoxycyclopropane,^{9,10} 1,2-dicyano-1,2-dicarbomethoxycyclopropane units.¹¹ In this work we investigated the polymerization behavior of another vinyl monomers containing multicyano-substituted cyclopropane. The present report describes the synthesis and polymerization behavior of *p*-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phenyl vinyl carbonate (3) and *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl vinyl carbonate (5). We now report the results of the initial phase of the work.

p-Formylphenyl vinyl carbonate 1 was prepared¹² by Schotten-Baumann method and condensed with methyl cyanoacetate or malononitrile to yield *p*-(2-cyano-2-carbomethoxy)vinylphenyl vinyl carbonate 2 and *p*-(2,2-dicyanovinyl)phenyl vinyl carbonate 4, respectively.^{13,14} *p*-(2,2,3-tricyano-3-carbomethoxycyclopropyl)phenyl vinyl carbonate 3 and *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl vinyl carbonate 5 were synthesized¹⁵ in high yields by cyclopropane formation from bromomalononitrile and 2 or 4, according to a variation of the Wideqvist reaction.¹⁶ The chemical structure of the compounds was confirmed by ¹H-NMR, IR spectra, and elemental analyses. Spectral data indicated that 2 and 3 were mixtures of the *cis*- and *trans*-isomer.

Compound 3 and 5 were quite stable when heated up to 100°C. Compound 3 and 5 did not homopolymerize with various catalysts such as AIBN, BPO, DTBP, BF₃, Et₃B, CH₃ONa, NaCN, and failed to secure a sample polymer polymer-



ized in vinyl-type so far. However, copolymerization of 3 or 5 with MMA (feed ratio by mol : 3/MMA = 1.0/1.0) using AIBN as an initiator at 65°C for 8 hr proceeded to form the corresponding copolymers in 80% yields.¹⁷ Structure of copolymers were determined by ¹H-NMR and IR spectra.¹⁸ A copolymer sample showed resonance peaks at 7.25-8.12 ppm attributable to aromatic protons of compound 3 in ¹H-NMR spectrum. The same copolymer sample showed strong absorption band at 2260 cm⁻¹ in IR spectrum indicating the presence of nitrile groups. These spectral data indicate that the monomer 3 or 5 is incorporated into the copolymers. The copolymer also showed a resonance peak of methyl group of MMA at 0.71-1.40 ppm in ¹H-NMR spectrum. In IR spectrum the strong absorption bands at 1762 cm⁻¹ and 1723 cm⁻¹ by carbonyl groups of MMA and compound 3 were exhibited. These spectral evidences indicate that the copolymer is composed of MMA and compound 3. The copolymer was soluble in acetone, but was not soluble in chloroform and diethyl ether. The inherent viscosities of copolymer were in the range of 0.15-0.20 dL/g in acetone at 25°C.

We are exploring further other features of the present copolymerization systems and the full accounts of the work will be reported shortly.

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- Compound 1: Yield=78%; $^1\text{H-NMR}$ (acetone- d_6) δ 4.62-5.21 (m, 2H), 6.96-7.35 (q, 1H), 7.36-7.65 (m, 2H), 7.83-8.14 (m, 2H), 10.01 (s, 1H); IR (neat) 1766, 1698 (C=O), 1650 (C=C) cm^{-1} .
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- Compound 2: Yield=50%; mp. 114-116°C; $^1\text{H-NMR}$ (acetone- d_6) δ 3.86 (s, 3H), 4.65-5.20 (m, 2H), 6.95-7.32 (q, 1H), 7.35-7.65 (m, 2H), 7.93-8.36 (m, 3H); IR (KBr) 2218 (CN), 1765, 1737, 1725 (C=O), 1646, 1609, 1596 (C=C) cm^{-1} .
Compound 4: Yield=65%; mp. 120-122°C; $^1\text{H-NMR}$ (acetone- d_6) δ 4.63-5.21 (m, 2H), 6.95-7.33 (q, 1H), 7.37-7.68 (m, 2H), 7.89-8.35 (m, 3H); IR (KBr) 2232 (CN), 1677 (C=O), 1653, 1594 (C=C) cm^{-1} .
- Compound 3: Yield=90%; mp. 117-119°C; $^1\text{H-NMR}$ (acetone- d_6) δ 3.96 (s, 3H), 4.33 (s, 1H), 4.57-5.23 (m, 2H), 6.95-7.33 (q, 1H), 7.34-7.67 (m, 2H), 7.68-8.12 (m, 2H); IR (KBr) 2253 (CN), 1757 (C=O), 1648 (C=C) cm^{-1} . Anal. Calcd for $\text{C}_{17}\text{H}_{11}\text{N}_3\text{O}_5$: C, 60.54; H, 3.29; N, 12.46. Found: C, 60.62; H, 3.35; N, 12.54.
Compound 5: Yield=92%; mp. 169-171 (dec); $^1\text{H-NMR}$ (acetone- d_6) δ 4.60-5.17 (m, 3H), 6.89-7.32 (q, 1H), 7.32-7.64 (m, 2H), 7.70-8.06 (m, 2H); IR (KBr) 2262 (CN), 1764 (C=O), 1654 (C=C) cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_8\text{N}_4\text{O}_3$: C, 63.16; H, 2.65; N, 18.41. Found: C, 63.25; H, 2.61; N, 18.50.
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- Copolymer composition estimated from $^1\text{H-NMR}$ spectrum: 3/MMA=22/78 (mol/mol).
- Spectral data of copolymer containing approximately 22 mol% of 3 and 78 mol% of MMA: $^1\text{H-NMR}$ (acetone- d_6 , 60 MHz) δ 0.71-1.40 (m, 3H), 1.65-2.48 (m, 4H), 3.27-4.15 (m, 7H), 4.28-4.57 (s, 1H), 7.25-8.12 (m, 4H); IR (KBr) 2260 (CN), 1762, 1723 (C=O) cm^{-1} .

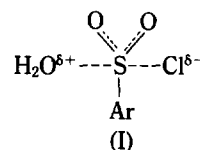
Theoretical Studies on the Substitution Reaction of Sulfonyl System: Hydrolysis of Methanesulfonyl Chloride in the Gas Phase

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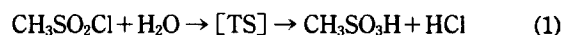
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Experimental studies on the hydrolysis or solvolysis of sulfonyl systems are numerous¹, but there seems to be no theoretical work reported on the intrinsic nucleophilic reactivity of sulfonyl system or tetracoordinate sulfur, except a few ground state analysis². From the experimental works of the hydrolysis of arylsulfonyl chloride, a trigonal bipyramidal structure was postulated for the $\text{S}_{\text{N}}2$ transition state, (I).



However, a four membered cyclic transition state, in which heavy atom reorganization(HAR) and proton transfer(PT) processes occur concertedly, should be considered in view of such transition state(TS) found for formaldehyde hydration in the gas phase³. In this transition state structure, an empty σ^* molecular orbital on sulfur-chlorine bond is available for the approaching nucleophile, and both entering and leaving groups will be in a plane perpendicular to the rest of the molecule, *i.e.*, a trigonal bipyramidal structure in addition to the four membered cyclic structure.

In this work, the hydrolysis reaction of methanesulfonyl chloride, eq. (1), was discussed theoretically by locating stationary points including transition state.



The Gaussian 92⁴ and MOPAC 6.0⁵ programmes were used throughout in this work for *ab initio* and semi-empirical molecular orbital calculations, respectively. The basis sets for the *ab initio* calculations were 3-21G* and 6-31G*, and hamiltonians for the semi-empirical calculations were AM1 and PM3⁶. It has been reported that the PM3 method successfully reproduces the heat of formation of hypervalent compounds without the use of *d* orbitals⁷, and parameters for the sulfur atom in the MOPAC program were revised⁵.

The transition state that corresponds to a saddle point on the 28-dimensional potential energy surface was characterized by confirming only one negative eigenvalue in the Hessian matrix.

Some optimized geometries of the system are summarized in Table 1, and a superimposed TS structure is shown in Figure 1 with the 6-31G* transition state structure and Pau-

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