Polymer Bulletin 1, 625-629 (1979)

Polymer Bulletin

Synthesis and Polymerization of 3-Methylenecyclobutene-1-Carbonitrile

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Introduction

3-Methylenecyclobutene and 1-methyl-3-methylenecyclobutene polymerize readily. (APPLEQUIST, ROBERTS 1956; WU, LENZ 1972). Cyclobutene-1-carbonitrile is a reactive monomer comparable to acrylonitrile in free radical polymerization (GALE et al. 1974). In view of the above, 3-methylenecyclobutene-1-carbonitrile should be a new highly reactive monomer.

Experimental

A three neck flask fitted with a mechanical stirrer, condenser, dropping funnel was charged with 1200 ml of dry chloroform, 165 g (2.06 moles) of dry pyridine, and 313.1 g (1.5 moles) of phosphorus pentachloride while under positive nitrogen pressure. Drop wise addition of 93.13 gm (1.00 mole) of 3-methylenecyclobutene-1-carbonitrile (CRIPPS, WILLIAMS, SHARKEY 1959) was done over a period of 2 hours. The reaction was refluxed with stirring for 96 hours. After cooling, the mixture was poured onto 2 kg of ice, separated, and the aqueous phase washed twice with ether. The combined organic fractions were washed with a saturated solution of potassium chloride, followed by a 10% solution of sodium carbonate. After drying over molecular sieves, the solvents were removed on a rotary evaporator. The residue was distilled to give 92.3 g (72%) of 1-chloro-3-methylenecyclobutane-1-carbonitrile **2**, b.p. 40°C (1.8 mm Hg).

Under positive nitrogen pressure, 150 ml of anhydrous ethyl ether, 0.05 g of 2,5-di-t-butylquinone and 13 g (0.10 moles) of 1-chloro-3-methylenecyclobutane-1-carbonitrile were placed in a dry flask containing a magnetic stirring bar. The flask was cooled to 5°C and 14.0 g (0.11 moles) of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) was added dropwise with stirring over 10 minutes. After stirring the reaction in an ice bath for 1.25 hours, the reaction mixture was filtered, returned to a flask, and kept at 5°C for 24 hours, during which more DBN-HCl had precipitated. The material was filtered and the ether removed on a rotary evaporator at room temperature. The residue was distilled at room temperature under vacuum by cooling the receiver flask in a Dry Ice-acetone bath. The fraction (b.p. 20°/(4-8 mm), 6.24 g (0.069 moles) was taken as a 69% yield of 2-methylenecyclobutene-1-carbonitrile (3).

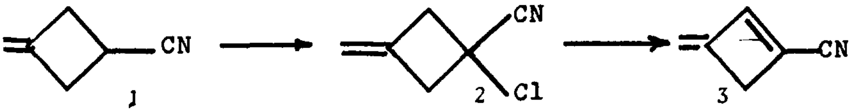
0170-0839/79/0001/0625/$01.00

nmr ($DCCl_3$) δ: 6.83 (s, 1 H); 5.14 (m, 1 H); 4.90 (m, 1 H);
3.27 (s, 2 H).
ir (neat): C-H, 3080, 2960 and 2925 cm^{-1}, m, m, and s;
C≡N, 2205 cm^{-1}, s; C=C, 1660 cm^{-1}, s.
UV (hexane); λmax = 253 nm, ε = 18,600
Mass spectra (10 EV); 91 m/e (P); calcd.: 91
Anal. calc'd for C_6H_5N: C, 79.10; H, 5.53; N, 15.37
Found C: 79.29; H, 5.54; N, 15.16

Free radical homo- and copolymerizations were done in a dry flask charged with the monomers and sulfolane and AIBN. The flask was capped with a rubber septum and flushed with argon, leaving a positive pressure in the flask. The flask was subjected to UV light for 20-72 hours at 40°C. The polymers were precipitated in methanol and worked up by standard methods except that the polymers were not heated in the drying process.

Results and Discussion

By treating 3-methylenecyclobutane-1-carbonitrile with phosphorus pentachloride, followed by DBN in ether, the new compound 3-methylenecyclobutene-1-carbonitrile 3 was synthesized in two easy steps. The chloride intermediate 2 was easier to purify if the reaction was allowed to proceed until all the starting material 1 had been consumed. Monomer 3 can be sufficiently purified by vacuum distillation at room temperature for polymerization studies. It is unstable at room temperature in the presence of air and gives an insoluble clear solid. Thus 3 was stored at -50°C, at which temperature it is crystalline.



Broad band and gated decoupled cmr spectra were taken (Table I) in deutero chloroform with a small amount of 2,5-t-butyl hydroquinone present to prevent the polymerization of 3. The absorptions of the quaternary carbons were very weak, as generally found.

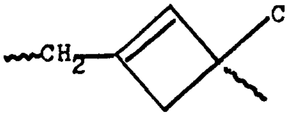
TABLE I

CMR Spectra of 3-Methylenecyclobutene-1-carbonitrile

Absorption	Shift(δ)	Number of Hydrogens	$J_{^{13}C\text{-}H}$	Assignment
1	40.05	2	144	$H_2\underline{C}$
2	108.19	2	160	$H_2\underline{C}{=}C$
3	119.26	-	-	$\underline{C}{=}C$
4	143.3	-	-	$\underline{C}{\equiv}N$
5	149.35	1	179	$H\text{-}\underline{C}$

When 3 was polymerized in sulfolane or in bulk with AIBN at 70°C, the polymers were always cross-linked and insoluble, although they swelled in DMF. Non-cross-linked polymers were obtainable in high yields from sulfolane solutions by using AIBN/UV initiation. The resulting polymers are insoluble in acetone, but soluble in DMSO and DMF, from which clear films were cast.

The structure of the polymer is considered to be 4, which comes from 1,5 addition. Other possible structures include 5 and 6 from 1,2 and 3,5 addition respectively.



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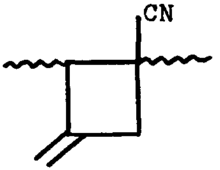

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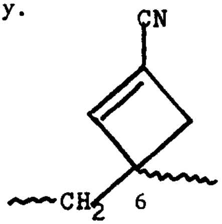

6

The ^{1}HMR spectrum of 4 has a peak at δ 6.10, assigned to the vinyl hydrogen. This compares with a peak at δ 6.0 in the spectra of cyclobutene (SILVERSTEIN, BASSLER, MORRILL 1974), δ 6.70 for cyclobutene-1-carbonitrile (GALE, CHERKOFSKY 1973), and 4.82 δ for 3-methylenecyclobutene-1-carbonitrile. If an appreciable amount of structure 6 were present in the polymer, then consideralbe crosslinking would be expected because of the reactivity of the remaining cyclobutenecarbonitrile group to free radical polymerization (GALE et al. 1974). A small amount of 3,5 addition may account for the crosslinking observed in the AIBN polymerization at 70°C.

TABLF 2

CMR spectra of poly-3-methylenecyclobutene-1-carbonitrile in DMSO-d6.

Absorption	Shift(δ)	Number of Hydrogens	$J_{^{13}C-H}$	Assignment
1	41.96	2	(a)	$-\underline{C}H_2-$
2	47.94	2	(a)	$H_2\underline{C}$
3	127.00	-	-	$\underline{C}=C$
4	136.5	1	184.8	$H-\underline{C}$
5	153.4	-	-	$-\underline{C}\equiv N$

a; obscured by solvent absorption.

Polymer 4 yellows rapidly around 170°C and the DSC scans shows an irreversible exotherm starting at 160°C.

Monomer 3 formed copolymers with styrene, p-methoxystyrene, methyl methacrylate and acrylonitrile. The copolymerizations were carried out in sulfolane containing AIBN and initiated by irradiating with UV light at 40°C. Copolymerization of isobutyl vinyl ether and 1 gave polymer that appeared from ^{1}HMR data to be the homopolymer of 3. Copolymerization results are given in Table 3.

TABLE 3

Copolymerization of 3-Methylenecyclobutene-1-carbonitrile

Comonomer	Feed ratio[a]	Yield[b]	η_{inh}[c]	Ratio[d]
p-Methoxy-styrene	1.0000/1	59%	0.83	1.2/1
Styrene	0.9753/1	65%	1.62	2.3/1
Methyl methacrylate	0.9915/1	34%	1.11	5.1/1
Acrylonitrile	0.9367/1	68.4%	1.26	20/1
Isobutyl vinyl ether	0.9985/1	57.7%	1.48	∞

a: moles 3/moles comonomer b: based on consumption of 3
c: in DMF at 30°C, g/100 cc d: moles 3 in polymer/moles comonomer in polymer.

The ratio of monomers in the copolymers were determined by ^{1}HMR and/or elemental analysis. In all of the copolymerizations, unreacted comonomers were detected by spectra in the methanol soluble fraction. Again all the copolymers are rich in the methylenecyclobutene monomer. The copolymers are all film-forming and soluble in acetone except for the case of isobutyl vinyl ether, which was considered to be homopolymer 4.

The above data shows that 3 is a very reactive new monomer.

ACKNOWLEDGMENTS

The authors wish to thank AMOCO Foundation Fellowship in Polymer Chemistry and the U.S. Army Research Office for financial support of this work.

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Received July 7, 1979