Macromolecules **1981**, *14*, 1833–1836

is changed to a *o* conformation, the steric energy of that conformer increases by about 3.8, 1.3, and 2.8 kcal/mol in syndiotactic, isotactic, and heterotactic sequences, respectively. Therefore, for the naphthyl group in P1VN, the π conformation is believed to be more stable than the *o* conformation.

The origin of the steric energies of the conformers is mainly attributed to the difference in the van der Waals (nonbonded) interaction energy and the bending energy of the bond angles. The optimized distance between the methine hydrogen and the hydrogen of the naphthyl ring in the same monomer unit was obtained as follows: in the *o* state, the distance from the hydrogen atom bonded to C(2) is 2.27 Å (1.02 kcal/mol), and in the π conformation the distance from the hydrogen atom bonded to C(9) is 2.16 Å (1.89 kcal/mol). If the interaction between the methine and naphthyl group is the only effective interaction within the same monomer unit, the *o* conformation is more stable than the π conformation. However, the *o* conformation imposes steric overlap between the hydrogens at C(9) in a rotating naphthyl ring and one of the methylene or α carbons which belongs to the adjacent monomer unit: the hydrogen atom on C(9) takes the center position of the two adjacent methylene hydrogens or the methylene hydrogen and the α-carbon atom in the adjacent monomer unit. In the optimized states, this hydrogen would be located at a position equidistant (2.25 Å) from the two methylene hydrogen atoms on each side. Consequently, the rotational freedom of the naphthyl groups should be strongly restricted in the *o* conformation. In the π conformation, the energy falls rapidly as the steric repulsions between the naphthyl groups are relieved by an increase in rotation of the side group. In the *o* conformation, as mentioned above, the energy does not fall as much as in the π conformation by the optimization process. An increase of the bending energy of the bond angle in the *o* conformation is also ascribed to the intense interaction between H(9) and the adjacent methylene hydrogen atom: the bending interactions of CH_2–αC–CH_2, $C_{aromatic}$–αC–CH_2 and $H_{methine}$–αC–CH_2 become important.

For the P2VN chain, the $\pi\pi\pi$ conformer may not always be of lowest energy: the $oo\pi$ conformer for isotactic and the $\pi\pi o$ conformer for heterotactic sequences are the most stable for the P2VN chain. The difference in steric energy between these conformers was about 0.91–0.26 kcal/mol. On the basis of the calculated results for the P2VN chain, which has the preferred conformation in the main chain, there were no appreciable nonbonded and bending interactions between the C(6) to C(9) atoms or the hydrogen atoms bonded to them (Figure 1) and the main chain (or the neighboring side groups). The extent of the interaction between the 2-naphthyl group and the main chain was almost of the same order as that in PS.

In order to estimate the curves of the potential energy as a function of the rotation angle of the aromatic ring for P1VN, P2VN, and PS, we used Tonelli's model.[12] The curves for P1VN did not resemble those for P2VN and PS, as we expected. On the other hand, the curves for P2VN correspond well to that for PS. The above results suggest that there is little conformational difference in the rotational states of P2VN and PS.

The conclusions obtained from Tables I and II are as follows: (a) In the P1VN chain, the π conformation is the preferred conformation. (b) In the P2VN chain, both the π and *o* conformations are stable conformations, the side-chain rotational state does not have a great influence upon the conformational stability of the main chain, and the circumstances are quite similar to those of PS.

Finally, it may be assumed that the difference of the RIS of the side groups between P1VN and P2VN probably leads to different solution behavior, as, for example, the ^{1}H NMR spectra or transition phenomena.

References and Notes

(1) Heller, J.; Miller, D. B. *J. Polym. Sci., Part A-1* **1967**, *5*, 2323.
(2) Frank, C. W.; Harrah, L. A. *J. Chem. Phys.* **1974**, *61*, 1526.
(3) Tazuke, S.; Banba, F. *Macromolecules* **1976**, *9*, 451.
(4) Irie, M.; Kamijo, T.; Aikawa, M.; Takemura, T.; Hayashi, K.; Baba, H. *J. Phys. Chem.* **1977**, *81*, 1571.
(5) Utracki, L. A.; Simha, R. *Makromol. Chem.* **1968**, *117*, 94.
(6) Helms, J. B.; Challa, G. *J. Polym. Sci., Part A-2* **1972**, *10*, 1447.
(7) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637.
(8) Wertz, D. H.; Allinger, N. L. *Tetrahedron* **1974**, *30*, 1579.
(9) Allinger, N. L.; Sparague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.
(10) Allinger, N. L.; Sparague, J. T.; Liljefors, T. *J. Am. Chem. Soc.* **1974**, *96*, 5100.
(11) Doskocilova, D.; Stokr, J.; Schneider, B.; Pivcova, H.; Kolinsky, M.; Petranek, J.; Lim, D. *J. Polym. Sci., Part C* **1967**, *16*, 215.
(12) Tonelli, A. E. *Macromolecules* **1973**, *6*, 682.

Polymerization and Copolymerization of Vinylisoxazole Derivatives

VINCENZO BERTINI,* MARCO POCCI, and
FILOMENA PROVENZANO

Dipartimento di Chimica dell'Università della Calabria,
87030 Arcavacata di Rende (Cosenza), Italy

ANGELA DE MUNNO

Istituto di Chimica Organica, Facoltà di Scienze M.F.N.
della Università, Via Risorgimento, 35, 56100 Pisa, Italy.

Received April 23, 1981

Introduction

Among polymerizations of vinyl heterocycles reported in the literature, studies involving isoxazole monomers[1] are rather seldom met. Nevertheless, macromolecules with pendant isoxazole residues could show interesting physical and chemical properties owing to the polarity, basicity, and coordinative power of such a ring. Besides, the ring's characteristic reactivity allows it to be transformed, by suitable reagents, into noncyclic 1,3-difunctional systems; i.e., the isoxazole nucleus could be a useful protecting group in the synthesis of polyfunctional polymers.

This paper deals with radical polymerization and copolymerization of 3,5-dimethyl-4-vinylisoxazole (I) and 5-vinylisoxazole (II) with styrene, acrylic acid, and other selected comonomers.

Results

Preparation and purification of reagents are reported in the Experimental Section.

Monomers I and II were homopolymerized and copolymerized with styrene and acrylic acid using azobis(isobutyronitrile) (AIBN) initiation. Other copolymerizations were carried out with comonomers selected on the basis of an approximate *Q–e* scheme to space out the isoxazole units as much as possible in order to prevent undesired interactions when the polymers are submitted to chemical transformations and to improve solubility in aqueous media at different pH values, keeping in mind that 3-unsubstituted isoxazole derivatives are unstable in the presence of bases. On account of this I was copolymerized with 4-vinylpyridine and 2-vinylpyridine and II was copolymerized with 2-vinylthiophene in the presence

0024-9297/81/2214-1833$01.25/0 © 1981 American Chemical Society

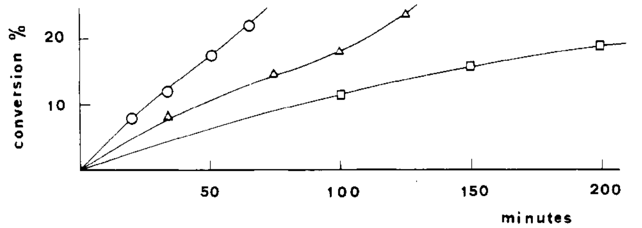

Figure 1. Bulk polymerization of 3,5-dimethyl-4-vinylisoxazole (I) (□), 5-vinylisoxazole (II) (○), and styrene (△) at 70 °C with 1% AIBN initiator.

of AIBN. Copolymerizations of I with styrene and acrylic acid were also carried out with acetyl peroxide (AcP) initiation. All reactions were performed in bulk under nitrogen at 40 °C with the exception of copolymerizations of II with 2-vinylthiophene and with acrylic acid which were conducted at 60 and 70 °C, respectively.

Values of conversion, in the 0–25% range, at 70 °C with 1% AIBN initiator for bulk homopolymerization of I, II, and styrene are plotted vs. time in Figure 1. Monomer I is slower and II faster than styrene to polymerize.

At high conversions bulk homopolymerization of both I and II shows an appreciable "gel effect".

Each homopolymerization or copolymerization of I or II yielded solid products still containing the isoxazole nucleus of the starting monomer as shown by the presence in the IR spectra of characteristic bands of trisubstituted or of 5-monosubstituted isoxazole (see Experimental Section). Each copolymerization yielded copolymers and not mixtures of homopolymers, and, in fact, attempts for selective extraction or separation by solubilization and partial reprecipitation with solvents always afforded products with practically an unchanged ratio of the intensities of the IR bands which are characteristic of the chromophores of the two different monomeric units. All isoxazole-containing homopolymers and copolymers with styrene, 4-vinylpyridine, 2-vinylpyridine, and 2-vinylthiophene, as well as homopolymers of such monomers prepared for comparison under the same conditions, showed birefringence under polarized light in a Kofler apparatus. Copolymers of I or II with acrylic acid showed birefringence for isoxazole mole fraction in the copolymer higher than 0.2.

Polymers and copolymers were further characterized by intrinsic viscosity measurements, vapor pressure or membrane osmometry, and gel permeation chromatography employing the "universal calibration method". The GPC columns and conditions used showed a fairly good resolution for homopolymer and copolymers of monomer II but were inadequate for samples of poly(3,5-dimethyl-4-vinylisoxazole) and copolymers rich in monomer I.

Some data obtained by osmometry and gel permeation chromatography on homopolymers of I and II and some of their copolymers with styrene are compared in Table I. Molecular weight and viscosity values of other polymeric samples are reported in the Experimental Section.

Homopolymers of I and II are soluble in methylene chloride, chloroform, dioxane, and acetone, slightly soluble in tetrahydrofuran and carbon tetrachloride, and very slightly soluble or insoluble in petroleum ether, cyclohexane, benzene, ethyl ether, ethanol, methanol, ethyl acetate, carbon disulfide, water, aqueous hydrochloric acid, and sodium hydroxide. Polymers with AcP initiation are generally a little less soluble than the analogous products obtained in the presence of AIBN. The homopolymer of II is a little more soluble than that of I in tetrahydrofuran, methanol, and ethyl acetate.

Homopolymers of I and II and their isoxazole-rich copolymers give brittle films by evaporation of saturated solutions.

The reactivity ratios, r_1 and r_2, were determined with

Table I
Intrinsic Viscosities in Chloroform at 25 °C and Molecular Weight Averages of Homopolymers of I and II and Their Copolymers with Styrene Prepared in Bulk at 40 °C with AIBN

polymer	mole fraction of isoxazole units in polymer	weight conversion, %	[η], mL/g	$\overline{M}_n$[a]	$\overline{M}_w$[b]	$\overline{M}_w/\overline{M}_n$[b]
homopolymer of I	1	11.42	26.6	5 000[c]		
copolymer I/styrene	0.696	10.66	33.8	34 000	117 000	1.69
copolymer I/styrene	0.303	6.33	66.7	67 000	170 000	1.93
homopolymer of II	1	7.20	62.8	11 000[c]	40 000	3.41
copolymer II/styrene	0.704	12.69	69.1	62 000	75 000	2.17
copolymer II/styrene	0.265	12.90	84.5	82 000	105 000	1.65

[a] Determined by membrane osmometry in chloroform at 37 °C unless otherwise noted. [b] Determined by GPC in chloroform at 25 °C using the universal calibration method. [c] Determined by vapor pressure osmometry in 1,2-dichloroethane at 37 °C.

Table II
Reactivity Ratios, r_1 and r_2, and Calculated Values of Q and e for Copolymerizations in Bulk of 3,5-Dimethyl-4-vinylisoxazole (I) and 5-Vinylisoxazole (II) at 40 °C with AIBN as the Initiator

monomer 1	monomer 2	r_1	r_2	Q_1	e_1	Q_2	e_2
styrene	I	3.06 ± 0.36	0.08 ± 0.01	1.00	−0.8	0.85	−1.99
		3.92 ± 0.30[a]	0.10 ± 0.01[a]				
acrylic acid	I	0.34 ± 0.08	0.04 ± 0.01	1.15	+0.77[b]	0.68	−1.31
		0.51 ± 0.06[a]	0.04 ± 0.01[a]				
4-vinylpyridine	I	0.96 ± 0.10	0.10 ± 0.02	0.82	−0.20[c]	0.98	−1.73
2-vinylpyridine	I	2.63 ± 0.36	0.06 ± 0.01	1.3	−0.5[c]	0.97	−1.85
styrene	II	0.17 ± 0.01	1.29 ± 0.10	1.00	−0.8	2.23	+0.44
acrylic acid[d]	II	0.11 ± 0.02	2.84 ± 0.30	1.15	+0.77[b]	4.66	−0.32
2-vinylthiophene[e]	II	0.72 ± 0.11	0.08 ± 0.02	3.00	−0.8[f]	2.90	+0.90

[a] With AcP initiator. [b] Reference 7. [c] Reference 8. [d] At 70 °C. [e] At 60 °C. [f] Reference 9.

a procedure based on the use of the differential copolymer equation[2,3] and calculated by the nonlinear least-squares method of Tidwell and Mortimer,[4] simplified by Carcano et al.[5] According to such computational treatment only the extreme points of the elliptical joint confidence limits are calculated; i.e., reference is made to a rectangle which circumscribes the elliptical area.

An improvement for accounting for monomer composition drift in the feed in the calculation method was deemed desirable, even when copolymerizations attain low conversions. This was done by introducing the arithmetic averages of the monomer feed mole fraction calculated with the use of the experimental data of copolymerization conversion according to Joshi.[6] With such simplifications the whole computer work is definitely light, the error limits are obtained in useful digital form, and loss of accuracy is insignificant with respect to the intrinsic experimental errors connected with the adopted procedure.

Collection of data for r_1 and r_2 determination was achieved through low-conversion copolymerization reactions and analysis of copolymers (see Experimental Section). Initially, several copolymerization reactions were carried out at different mole fractions of the monomers in the feed in order to estimate crude values of r_1 and r_2 and locate through them the "best" two values for the initial mole fractions of the monomers.[4] Other reactions were then achieved on initial monomer mixtures gathered around such compositions.

The reactivity ratios, r_1 and r_2, and the Alfrey–Price Q and e values are compared in Table II.

Discussion

The facile radical-initiated polymerization of monomers I and II and copolymerization with some vinyl monomers have been demonstrated.

With AcP in place of AIBN initiator, molecular weights under the same conditions are a little higher, in accordance with a greater propagation rate with AIBN.

Homopolymerization conversions vs. time (Figure 1) give the indication that monomer I is less and monomer II more reactive than styrene. The presence of two methyl groups "ortho" to the vinyl group in the monomer I is reminescent of 2,6-dimethylstyrene, which is known[10] to be much less reactive than styrene. Nevertheless, while the behavior of such an olefin may be correlated with its steric hindrance (twist angle 55°[11]), as far as monomer I is concerned electronic effects probably play an important role, too. Monomer I in fact contains a pentaatomic ring with a rather low aromatic stabilization which easily undergoes distortions of bond angles besides those of bond distances[12,13] and should permit nearly coplanar preferred conformations of the heterocycle and the vinyl group. Moreover, monomer I is remarkably more electron rich than styrene, in agreement with the e values (Table II), the presence of two methyl groups, and the reactivity of the isoxazole system. It is well-known in fact that the position 4 of such a ring is the only reactive one toward electrophilic reagents.

Monomer I follows the Q–e scheme better than monomer II. Q values indicate that monomer I is less conjugated than monomer II, in accordance with the fewer resonance structures which may be drawn for the delocalization of the radical. Monomer II reveals a polarity (see e values) dependent on the nature of the comonomer, in agreement with a rather long conjugated and poorly aromatic system characterized by high polarizability.

It is instructive to examine the obtained values of r_1 and r_2. Monomer I is less reactive toward benzyl radical ($1/r_1 = 0.33$, M_1 being styrene) than monomer II ($1/r_1 = 6.02$). In each examined copolymerization, monomer I is less reactive toward its radical than toward the radical of the comonomer ($r_2 < r_1$), in agreement with polymer chains where isoxazole units tend to be spaced out by comonomer units. On the contrary, monomer II is more reactive toward its radical than toward the radical of the comonomer in the copolymerization either with styrene or with acrylic acid. 2-Vinylthiophene reverses this trend, making the production of copolymers possible where isoxazole units of II tend to be spaced out.

The probability of finding sequences of two contiguous isoxazole units in the copolymer chain, which could be responsible for undesired interactions when copolymers are submitted to chemical transformation of their isoxazole rings,[14,15] has been calculated according to Price[16] as a function of the monomer feed mole fraction. For the copolymerizations with AIBN initiator a safeguard against undesired interactions, corresponding, for instance, to 0.1% probability of finding two contiguous isoxazole units, is obtained with the following values of the mole fraction of isoxazole monomer in the initial feed: for monomer I, less than 0.175 (0.062) with styrene, 0.109 (0.209) with acrylic acid, 0.099 (0.093) with 4-vinylpyridine, 0.184 (0.074) with 2-vinylpyridine; for monomer II, less than 0.100 (0.119) with 2-vinylthiophene, 0.012 (0.065) with styrene, and 0.006 (0.052) with acrylic acid (values in parentheses are the corresponding instantaneous mole fractions of the isoxazole units in the copolymer). The low safeguard content of II in the initial feed of copolymerization with styrene or acrylic acid confirms the inadequacy of such copolymers in using them in chemical transformations under controlled conditions.

Experimental Section

Viscosities were measured in chloroform at 25 °C with a Desreux-Bishoff viscometer. Gel permeation chromatograms were run in chloroform at 25 °C on a Waters Model ALC/GPC-202 equipped with μ-Bondagel columns E500, E300, and E125, using a flow rate of 0.6 mL/min; results were treated by using the universal calibration method. Number averages of molecular weight, $\bar{M}_n$, were determined at 37 °C in chloroform or 1,2-dichloroethane by Knauer vapor pressure and membrane osmometers. IR spectra were recorded with a Perkin-Elmer 377 spectrophotometer. Microanalyses were performed by Laboratorio di Microanalisi, Facoltà di Farmacia, Università di Pisa (Italy), or by Analytische Laboratorien Elbach (West Germany). Melting points were determined as birefringence disappearance under polarized light by a Kofler apparatus; the heating speed near the melting point was slower than 0.5 °C/min; the reproducibility was within 1 °C.

Monomers. 3,5-Dimethyl-4-vinylisoxazole[17] (I) and 5-vinylisoxazole[18] (II) were prepared as previously reported and further purified prior to use by fractional column distillation at reduced pressure under nitrogen in the presence of hydroquinone. Both showed a single peak by GLC on a 1.75-m column of 10% poly(propylene glycol) on CWS at 130 °C.

Commercial acrylic acid and 4-vinylpyridine were purified by fractional column distillation at reduced pressure under nitrogen in the presence of hydroquinone for the first and of KOH pellets for the second.

Commercial styrene was stirred with aqueous KOH, washed with water, dried over sodium sulfate, and fractionated at reduced pressure under nitrogen in the presence of calcium hydride.

2-Vinylthiophene was prepared according to Emerson et al.[19] and further purified by fractional column distillation at reduced pressure under nitrogen in the presence of 1-nitroso-2-naphthol.

2-Vinylpyridine was prepared according to Winterfeld et al.[20] and further purified by fractional column distillation at reduced pressure under nitrogen in the presence of KOH pellets.

Homopolymerizations and Copolymerizations. Polymer-

Table III
Intrinsic Viscosities in Chloroform at 25 °C and Number-Average Molecular Weights by Membrane Osmometry in Chloroform at 37 °C of Polymers of I and II

polymer (initiator; T, °C)	weight conversion, %	mole fraction of isoxazole units in polymer	[η], mL/g	$\overline{M}_n$
homopolymer of I (AcP; 40)	6.93	1	14.6	8 000 [a]
copolymer I/styrene (AcP; 40)	8.93	0.738	25.4	27 000
copolymer I/styrene (AcP; 40)	4.73	0.268	61.8	112 000
copolymer I/4-vinylpyridine (AIBN; 40)	7.98	0.397	100.3	73 000
copolymer I/2-vinylpyridine (AIBN; 40)	21.95	0.213	82.6	263 000
copolymer II/2-vinylthiophene (AIBN; 60)	8.65	0.108	14.6 [b]	20 000 [b]

[a] Determined by vapor pressure osmometry in chloroform at 37 °C. [b] In THF.

ization experiments were carried out in bulk under a nitrogen atmosphere after three freeze–thaw degassing cycles, using azobis(isobutyronitrile) (AIBN) or acetyl peroxide (AcP) as initiator, in 15-mL sealed Pyrex vials stirred in a thermostatic bath.

Commercial AIBN was crystallized from methanol, while AcP was used without further purification.

Polymers obtained by low conversion were precipitated by pouring the reacting mixture into petroleum ether or diethyl ether. In all cases crude polymer samples were purified by two cycles of dissolution in dichloromethane and precipitation into petroleum ether. Rather insoluble copolymers containing acrylic acid were purified by reflux in petroleum ether. Purification was achieved by maintaining samples under vacuum at 45 °C for 24 h. Homopolymers and copolymers obtained by this procedure are white or light yellow soft powders.

The copolymerization reactivity ratios were determined by an average of 18 low-conversion copolymerization experiments for the couples of monomers reported in Table II. The composition of the copolymers was determined by nitrogen analysis, with the exception of the copolymers with 2- and 4-vinylpyridines, which were subjected to oxygen analysis.

Poly(3,5-dimethyl-4-vinylisoxazole) (conversion 11.42%; mp 218 °C) shows IR bands in KBr characteristic of a trisubstituted isoxazole nucleus at 1627, 1490, 1444, 1425, 1013, and 899 cm^{-1}. Analogous bands are contained also in the IR spectrum of each examined copolymer of I. Other intense bands of the homopolymer are at 2934, 1310, and 1197 cm^{-1}.

Poly(5-vinylisoxazole) (conversion 8.56%, mp 140 °C) shows IR bands in KBr characteristic of the isoxazole nucleus monosubstituted in the 5 position at 1591, 798, and 624 cm^{-1}. Analogous bands are found in the IR spectrum of each examined copolymer of 5-vinylisoxazole. Other bands of the homopolymer are at 3127, 2935, 2860, 1573, 1368, 1335, 1241, 1179, 1067, 1035, 917, and 875 cm^{-1}.

Table III shows intrinsic viscosities and molecular weights of some polymers of I and II; other data are reported in Table II.

Acknowledgment. This work was supported by C.N.R., Roma.

References and Notes

(1) Sumimoto, S.; Ueda, N.; Imoto, M. *Kogyo Kagaku Zasshi* **1963**, *66*, 1505. Iwakura, Y.; Toda, F.; Suzuki, H.; Kusakawa, N.; Yagi, K. *J. Polym. Sci., Part A* **1972**, *10*, 1133.

(2) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.

(3) Van der Meer, R.; Linssen, H. N.; German, A. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2915.

(4) Tidwell, P. W.; Mortimer, G. A. *J. Polym. Sci., Part A* **1965**, *3*, 369.

(5) Carcano, D.; Modena, M.; Ragazzini, M.; Pilati, O. *Chim. Ind. (Milan)* **1971**, *53*, 547.

(6) Joshi, R. M. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1231.

(7) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook"; Wiley: New York, 1975.

(8) Young, L. J.; Kennedy, C. C. *High Polym.* **1964**, *18*, Appendix B.

(9) Walling, C.; Briggs, E. R.; Wolfstirn, K. B. *J. Am. Chem. Soc.* **1948**, *70*, 1543.

(10) Yamamoto, S.; Tatsumi, M. *Nippon Kagaku Kaishi* **1976**, 994. *Chem. Abstr.* **1976**, *85*, 78404.

(11) Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 196.

(12) De Munno, A.; Bertini, V.; Vaglini, U.; Cetino, M. S.; Pino, P. *Atti Soc. Toscana Sci. Nat., Pisa, Mem., Ser. A* **1969**, *76*, 350.

(13) De Munno, A.; Ceccarelli, G.; Bertini, V. *Atti Soc. Toscana Sci. Nat., Pisa, Mem., Ser. A* **1969**, *76*, 408.

(14) Bertini, V.; Pelosi, P.; De Munno, A. *J. Heterocycl. Chem.* **1972**, *9*, 741.

(15) Krishaswami, P.; Yadav, D. P. *J. Appl. Polym. Sci.* **1976**, *20*, 1175.

(16) Price, F. P. *J. Chem. Phys.* **1962**, *36*, 209.

(17) Bertini, V.; De Munno, A.; Pocci, M. *J. Chem. Soc., Perkin Trans. 1* **1976**, 570.

(18) Bertini, V.; De Munno, A.; Pelosi, P.; Pino, P. *J. Heterocycl. Chem.* **1968**, *5*, 621.

(19) Emerson, W. S.; Patrick, T. M., Jr. "Organic Synthesis"; Wiley: New York, 1963; Collect. Vol. IV, p 980.

(20) Winterfeld, K.; Heinen, C. *Justus Liebigs Ann. Chem.* **1951**, *573*, 85.