

ANIONIC POLYMERIZATION OF PROPIOLONITRILE

M.J. BENEŠ and J. PEŠKA

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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The polymerization of propiolonitrile was initiated with butyllithium, lithium cyanide, lithium alkoxides and tertiary amines. In the case of butyllithium transmetalation is the first step, cyanocetylde thus formed being the initiator proper. The other initiators initiate the polymerization directly. Polymers containing a reactive tertiary amine are grafted with propiolonitrile. The schemes of polymerization mechanism proposed so far are discussed and completed by the findings of this work.

The anionic polymerization of propiolonitrile, propiolanhydride, propiolamide and methyl propiolate giving rise to linear polymers with conjugated double bonds in the main chain has been described in the literature¹. In this work an attempt has been made to elucidate some aspects of the polymerization of propiolonitrile, and the initiation step in particular.

EXPERIMENTAL

Propiolonitrile was obtained by dehydration of propiolamide with phosphorus pentoxide². The preparation of butyllithium, purification of tetrahydrofuran and the polymerization technique have been described earlier³. Lithium cyanide was obtained by a reaction of butyllithium with hydrogen cyanide⁴. Triethyl amine was freed from traces of primary and secondary amines with tosyl chloride. *p*-Chlorobenzyl dimethyl amine was obtained by alkylation of dimethyl amine with *p*-chlorobenzyl chloride⁵ and purified similarly to triethyl amine.

After the polymerization of propiolonitrile and its reaction with lithium alkoxides the products were isolated by evaporating the solvent and unreacted monomer *in vacuo*; the adducts RO—CH=CH—C≡N (I) and (RO)₂CHCH₂—C≡N (II) (R being CH₃ or C₂H₅) were separated by distillation *in vacuo* and identified according to the physical constants and infrared spectra. The grafting of polyamines with propiolonitrile was carried out so that an excess of propiolonitrile was added to a solution of polymeric initiator in tetrahydrofuran or in dimethylformamide; the excess of the monomer was removed *in vacuo* at room temperature after 5 h, the polymer extracted with acetone and methanol in order to remove the polypropiolonitrile that might be present in the mixture, and analyzed.

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The molecular weights of polymers were determined by the end group method; a solution of polymers in methanol was converted into the H form on a cation exchanger (Zerolit 225) and titrated potentiometrically with a standard alkali solution. The residual alkalinity of the polymers was determined by potentiometric titration of acetonitrile solutions with perchloric acid. The molecular weights of the dimer of propionitrile and its adducts with alkoxides were determined by the VPO method. The IR and NMR spectra were recorded with a Zeiss UR 10 and an NMR JEOL-60 apparatus respectively.

RESULTS

Typical examples of polymerizations are summarized in Table I. The polymers are partly separated from the tetrahydrofuran solution during the polymerization, but they are soluble in polar organic solvents (methanol, ethanol, acetone, acetonitrile, *etc.*) and with the exception of polymers initiated with tertiary amines, also in water. Similarly to cases described earlier³, the conversion of the monomer into the polymer was found to increase with the initiator monomer ratio. For example, in the case of initiation with triethyl amine at an initial concentration of propionitrile of 0.861 mol/l the conversion at 0°C is 32.1% and 75.3%, if the molar initiator monomer ratio is 0.0342 and 0.100 respectively.

The polymerization rate with tertiary amines depends on the initiator used. The conversion for triethyl amine is 74.9% after three hours; for 4-chlorobenzyl dimethyl amine it is 54% after 4.5 h and 68% after 24 h. In the case of the latter amine, a side product was also isolated and identified by its infrared spectrum (960, 1270, and 2260 cm^{-1}) and molecular weight (103, VPO method in acetone) as a dimer

$$\begin{array}{c} \text{H} \\ | \\ \text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}=\text{C}-\text{C}\equiv\text{N} \quad (\text{III}) \quad (\text{m.p. } 76.5^\circ\text{C}). \\ | \\ \text{H} \end{array}$$

amine is used as initiator.

It follows from the infrared spectra that the polymerization takes place on the $-\text{C}\equiv\text{C}-$ triple bond, while the nitrile groups remain unchanged (2200 cm^{-1}). The spectra of polymers prepared by various initiators differ in the region of aliphatic $\text{C}-\text{H}$ vibrations near 2950 cm^{-1} . If butyllithium is used as initiator, the butyl group is not bonded in the polymer, while if alkoxides or tertiary amines are used, the polymer contains an alkoxy or trialkylammonium group respectively. The binding of the tertiary amine in the polymer was also proved by initiation with *p*-chlorobenzyl dimethyl amine and by determination of chlorine in the polymer thus obtained.

Initiation with polymeric amines (Table II) gives rise to grafted polymers which are insoluble in common solvents. Insoluble polymers are also formed by grafting of copolymers, particularly of those of 4-vinylpyridines, where the region of partial solubility is limited to a small portion of the lowest content of base in the polymeric initiator.

TABLE I

Reactions of Propiolonitrile

Initial monomer concentration 1.0 mol/l, initiator concentration 0.1 mol/l, reaction time 3 h at 0°C.

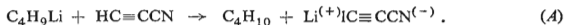
Initiator	Solvent	Polymer		Adducts g I, II ^a
		conversion, %	mol. weight	
Triethylamine	tetrahydrofuran	75	1 790	—
Lithium cyanide	tetrahydrofuran	75	1 320	—
Butyllithium	tetrahydrofuran	75	1 510	—
Lithium methoxide	methanol	0	—	1.74
Lithium ethoxide	ethanol	6.5	—	1.85
Lithium tert-butoxide	tert-butylalcohol ^b	82	960	0

^a cf. Experimental; amount given for 1.22 g of propiolonitrile. ^b Reaction at 25°C.

DISCUSSION

The ability of propiolonitrile to polymerize with anionic⁶⁻¹⁰ and complex¹¹⁻¹² initiators is known in the literature. In all cases the formation of low-molecular weight linear polymers has been described; if complex initiators are used, these polymers are accompanied by a cyclic trimer, *viz.*, trimellitonitrile. A hypothesis has been forwarded that the presence of a relatively acidic acetylenic hydrogen atom interferes with the anionic polymerization carried out with strongly basic initiators, and that cyanoacetylides produced by competitive reaction are not able to initiate further polymerization⁸. Our results show, however, that the polymerization caused by butyllithium proceeds just *via* this intermediate step. The fact that transmetalation occurs preferentially is indicated by high yields of cyanoacetylide obtained in a nonpolar medium¹³. Polymerization accompanied by deepening of the colour of the reaction mixture was observed as a secondary phenomenon and could be avoided. The ability of alkaline acetylides to initiate polymerization of some mono-substituted acetylenic hydrocarbons has also been described in an earlier paper¹⁴. In this case it was the effect of the strongly polar solvent—dimethylsulphoxide, which caused the dissociation of ionic pairs of the growth centre and thus the polymerization itself. In the case of propiolonitrile the favourable effect of the electronegative nitrile group comes to the fore. The electrophilic property of the $\text{—C}\equiv\text{C—}$ bond becomes considerably increased, which in its turn accelerates and facilitates the addition of the monomer to the growth centre. Nitriles on the polymer support the dissociation on the growth centre to such a degree¹⁵ that polymerization takes place even in a nonpolar medium.

Transmetalation is the first step during initiation with a strong anionic initiator:



A somewhat different case appears during initiation with alkaline alkoxides.

TABLE II

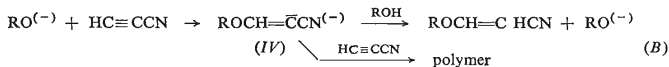
Grafting of Polymeric Amines with Propiolonitrile (M)

Base content ^a mol%	Extent of reaction mol M reacted per mol of base	Solubility ^b
Poly(2-vinylpyridine)		
100	2.6	—
Poly(4-vinylpyridine-co-styrene)		
2.8	9.8	+
5.6	4.6	—
7.3	3.7	—
12.5	3.0	—
100	2.4	—
Poly(4-vinylpyridine-co-methyl methacrylate)		
3.4	2.0	+
13.7	4.4	—
35.9	1.6	—
100	2.1	—
Poly(4-vinylpyridine-co-2-hydroxyethyl methacrylate) ^c		
6.6	0.4	—
17.0	1.6	—
37.2	1.2	—
Poly(2-dimethylaminoethyl methacrylate-co-methyl methacrylate)		
1.1	6.7	++
5.1	5.4	++
100	5.2	—

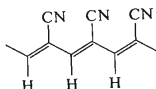
^a Initial content determined by potentiometric titration with perchloric acid in acetic acid¹⁸.

^b Meaning of symbols: — separates from solution during reaction, insoluble in organic solvents, + remains in solution during reaction, does not dissolve any more after precipitation, ++ soluble in acetone, THF, DMFA, insoluble in methanol. ^c Slightly crosslinked gel was used as polymer initiator; grafted in swollen state (DMFA).

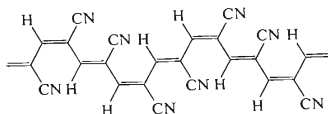
According to the literature⁸, with sodium methoxide in dimethylformamide the molecular weight appears to be rather insensitive to the amount of methanol present. Under conditions used by us this phenomenon could not be observed. Initiation with 0.1M lithium methoxide in methanol does not give rise to a polymer, but only to a mixture of adducts *I cis* and *II* (Table I). At a higher concentration of sodium methoxide in methanol, adduct *II* is formed² in a high yield. The use of lithium ethoxide in ethanol leads to a partial formation of the polymer, besides both adducts. On the other hand, lithium tert-butoxide in tert-butyl alcohol yields almost exclusively a polymer and only traces of adducts. Polymerization and addition have a common first step,



Thus, the adduct is a product of the transfer reaction to alcohol. Such transfer of an anion is possible only if the pK_a of the alcohol is lower or close to that of an acid conjugated to anion *IV*. A situation involving close pK_a values arises for ethanol where both the adduct and the polymer are formed. Transfer to alcohol becomes still less likely after the addition of further molecules of propiolonitrile, since the addition of further monomer units reduces pK_a of the polymer to a value below pK_a of the alcohol owing to the effect of electronegative nitrile groups on the conjugated chain.



VI



VII

The unusually strong electrophilic character of the $\text{—C}\equiv\text{C—}$ bond in propiolonitrile is also reflected in the fact that the initiation can be performed by such bases as lithium and sodium cyanides or even potassium thiocyanide⁷. The initiation efficiency is very low, however, and a polymer is formed, even if the propiolonitrile thiocyanide ratio is two. Also in the polymerization initiated with butyllithium, lithium cyanide or lithium tert-butoxide is the initiation far from quantitative; only about 60% of initiator is utilized for the initiation, judging by the titration of the residual basicity.

For polymerizations initiated with tertiary amines the amine was found to be chemically bonded in the polymers. The initiation step consists in an addition giving

rise to a zwitterion $R_3\overset{+}{N}CH=\overset{-}{C}CN$ (V), the same that is known as an intermediate of a reaction of the tertiary amine with chloroacrylonitrile¹⁶. The nature of growth is somewhat unclear in this case, since it would be necessary to assume that in an isolated molecule the distance between opposite charges increases. The possibility that the anion may move closer to the quaternary nitrogen atom owing to tautomerism would lead to branching, which however could not be proved. It seems more likely therefore that the electrostatic charges are compensated for intermolecularly, for instance by the formation of dimers of the type $\overset{+}{\sim}\overset{-}{\sim}$. This view is corroborated by the observed loss of solubility of copolymers containing a tertiary amine during grafting with propiolonitrile (Table II).

From the steric viewpoint, addition of the monomer to form the *cis* and *trans* structure may take place here; in the case of a planar configuration of the main chain simple bonds may also have a *transoidal* or *cisoidal* configuration. Both these processes lead to a high number of possible stereoisomers. Indeed, a majority of the expected isomers was isolated for oligomers of phenylpropiolonitrile¹⁷. Polypropiolonitrile was divided into coloured zones by means of TLC⁸. Elution chromatography of the sample in an arrangement described earlier¹⁷ gave an orange, red and brown zone. The NMR spectra of polymers initiated with butyllithium exhibit only one type of hydrogen atoms; in polymers initiated with lithium cyanide there are two types of hydrogen atoms, roughly in a 1 : 1 ratio. The former condition is fulfilled by *trans-transoidal* configuration (VI), the latter one by the *trans-transoidal-cis-transoidal* configuration (VII):

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REFERENCES

1. Beneš M. J., Janić M., Peška J.: Chem. listy 64, 1094 (1970).
2. Murahashi S., Takizawa T., Kurioka S., Maekawa S.: Nippon Kagaku Zasshi 77, 1689 (1956).
3. Beneš M. J., Peška J., Wichterle O.: J. Polymer Sci. C16, 555 (1967).
4. Johns I. B., DiPietro H. R.: J. Org. Chem. 29, 1970 (1964).
5. Eliel E. L., Ferdinand T. N., Herrmann M. C.: J. Org. Chem. 19, 1693 (1954).
6. Manassen J., Wallach J.: J. Am. Chem. Soc. 87, 2671 (1965).
7. Manassen J., Wallach J.: International Symposium on Macromolecular Chemistry, Tokyo 1966, Preprint 2-1-15.
8. Wallach J., Manassen J.: J. Polymer Sci. A-1, 7, 1983 (1969).
9. Mac Nulty B.: J. Polymer 7, 275 (1966).
10. Hankin A. G., North A. M.: Trans. Faraday Soc. 63, 1525 (1967).
11. Misono A., Noguchi H., Noda S.: International Symposium on Macromolecular Chemistry, Tokyo 1966, Preprint 1-2-01.
12. Misono A., Noguchi H., Noda S.: J. Polymer Sci. B, 4, 985 (1966).
13. Kloster-Jensen E.: Acta Chem. Scand. 18, 1629 (1964).

14. Kříž J., Beneš M. J., Peška J.: *This Journal* 32, 4043 (1967).
15. Peška J., Beneš M. J.: *This Journal* 38, 2595 (1973).
16. Scotti F., Frazza E. J.: *J. Org. Chem.* 29, 1800 (1964).
17. Janić M., Beneš M. J., Peška J.: *Makromol. Chem.* 138, 99 (1970).
18. Tamikado T.: *J. Polymer Sci.* 43, 489 (1960).

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