Polymer Bulletin 3, 593-596 (1980)

Polymer Bulletin

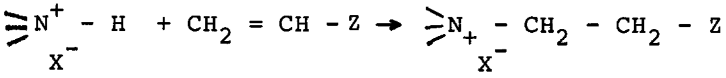
A Method of Obtention of N Substituted Quaternary Ammonium Salts Supported by a Polymeric Chain

Taghi Taghizadeh, Claude Cazé and Claude Loucheux

Laboratoire de Chimie Macromoléculaire, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cédex, France

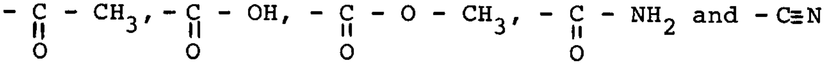
Summary

Starting from tertiary amine polymers the reaction can be written in two steps 1) quaternization of the amine group by acid halide 2) addition of an electrophylic ethylenic reagent on the quaternary ammonium salt :



$$\underset{X^{-}}{\geq N^{+}} - H + CH_2 = CH - Z \rightarrow \underset{X^{-}}{\geq N_{+}} - CH_2 - CH_2 - Z$$

X^{-} is Cl^{-} or Br^{-}. $\geq N$ is the tertiary amine supported by the polymers. Tertiary amine group tested are : pyridine, pyrazine, quinoleine, quinoxaline and N dimethyl phenyl. Z is an attracting group as :



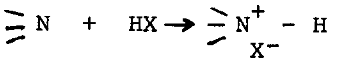
$$-\underset{\underset{O}{\|}}{C} - CH_3,\ -\underset{\underset{O}{\|}}{C} - OH,\ -\underset{\underset{O}{\|}}{C} - O - CH_3,\ -\underset{\underset{O}{\|}}{C} - NH_2 \text{ and } -C\equiv N$$

Introduction

Quaternary ammonium polymers have many industrial applications. These type of polymers are generally obtained by quaternization of a tertiary amine group by an alkyl halogenated derivative (MORCELLET-SAUVAGE and LOUCHEUX 1975). We proposed a new way of obtaining such compounds. This method is the application to polymeric reagents (GHESQUIERE et al 1975, TAGHIZADEH et al 1979) of the reaction between an electrophilic ethylenic group and a protonated tertiary amine (LE BERRE and DELACROIX 1973, DOWENKO 1960).

Experimental

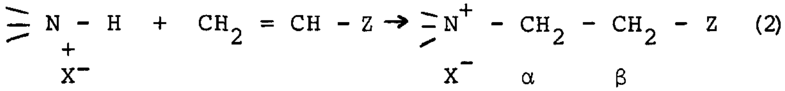
Starting form tertiary amine polymers the reaction can be written in two steps :
1°) Quaternization of the tertiary amine polymer with an acid halide :



$$\geq N + HX \rightarrow \underset{X^{-}}{\geq N^{+}} - H \qquad (1)$$

0170-0839/80/0003/0593/$01.00

2°) Addition of the electrophilic ethylenic reagent on the quaternary ammonium salt :



$$\underset{X^-}{\underset{+}{\geq N}} - H + CH_2 = CH - Z \rightarrow \underset{X^-}{\geq N^+} - \underset{\alpha}{CH_2} - \underset{\beta}{CH_2} - Z \qquad (2)$$

The two steps were carried out successively in a solvent of the protonated polyamine (without any separation of the protonated polyamine). The second step was carried out at 70°C during variable times (1 to 24 hours) with an excess of the ethylenic reagent. Modified polymers were twice precipitated then characterized by ^1H NMR (Varian T60) and IR (Perkin Elmer 257). NMR spectra were recorded from D_2O, CD_3OD or $CDCl_3$ solutions using dioxane or TMS as internal standard . IR spectra were recorded from films. Generally we could note in the ^1H NMR spectra the characteristic resonance of the α and β - CH_2 - group (as defined in equation 2), and in the IR spectra the absorption band characteristic of the Z function. Quantitative analysis of modified polymers was made by a potentiometric determination of the X^- content and a conductimetric determination of free amino groups (TAMIKADO 1960).

Tertiary amine polymers tested were : poly(4 vinyl pyridine)(P4VP), poly(2 vinyl pyridine)(P2VP), poly(2 methyl 5 vinyl pyridine)(P2M5VP), poly(2 vinyl pyrazine)(P2VPY), poly(2 vinyl quinoleine)(P2VQ), poly (phenyl quinoxaline)(PPQ), poly(dimethyl amino styrene) (PDMAS). All polymers were obtained by conventional radical polymerization except PPQ and PDMAS which were commercial products.

Ethylenic reagents were : vinyl methyl cetone (VMC), acrylic acid (AA), methyl acrylate (MA), acryl amide (AM) and acrylonitrile (AN). All these products were commercial.

Results and Discussion

In a first time we examine the possibility of addition of the different ethylenics on P4VP. Results are summarized in Table 1.

A quantitative addition is easy for VMC and AM but we note a partial addition in the case of MA and AA, and no reaction at all with AN.

In a second time we studied the addition of VMC to a series of polymers containing different tertiary amine groups. In this case the first step of the reaction was arbitrarily limited to 50 %, 25 % in the case of P2VPY and PPQ (experimentally we note that the rate of the second step decreases at high percentage of protonated amine). The second step of the reaction was performed in different solvents : methanol (MeOH), dimethyl formamide (DMF), tetramethylsulfone (TMS) and chloroform, depending on the polymer studied. The results obtained are reported in Table 2 (the percentage of addition refers to the protonated amine).

TABLE I

Modification of P4VPH^+ Cl^- by some ethylenic reagents in methanol

Ethylenic		VMC	AM	AA	MA	AN
% of addition		95	95	42	40	0
IR absorption band of the Z group in cm^{-1}(a)		1710	1670	1710	1725	-
(b)	β	3.4-3.7	3.4-3.8	-0.93	- 1	-
	α	6.1	6.0	2.3	2.6	

a) absorption of the $\geq C = O$ group fixed on polymer

b) ^1H resonance of α and β - CH_2 - group as defined in scheme (2) in the case of VMC and AM:solvent CD_3OD reference TMS. in the case of AA and MA:solvent D_2O reference dioxane.

TABLE II

Reactions of some polymers with VMC

Polymer	Solvent	% of addition	IR absorption of the $\geq$C=O group in cm^{-1}	(a) β
P2M5VP	MeOH	58	1710	(b) 3.3
P2VPY	MeOH	90	1720	(b) 3.5
P2VP	DMF	82	1710	(c) -0.9
P2VQ	DMF	30	1720	(b) 3.9
PPQ	$CHCl_3$	63	1710	(d) 3.4
PDMAS	TMS	98	1730	(c) -1

(a) ^1H NMR resonance of the β - CH_2 - group as defined in scheme (2) (the α resonance is generally masked)

(b) solvent : CD_3OD reference TMS

(c) solvent : D_2O reference dioxane

(d) solvent : $CDCl_3$ reference TMS

Conclusion

We have shown that the obtention of N substitued quaternary ammonium salts is possible by direct addition of an electrophilic ethylenic on a protonated polyamine.

References

DOWBENKO, R. : J. Org. Chim. 25, 1123 (1960).
LE BERRE, A. and DELACROIX, A. : Bull. Soc. Chim. 540 (1973).
MORCELLET-SAUVAGE,J. and LOUCHEUX,C. : Makromol. Chem. 176, 315 (1975).
TAGHIZADEH, T., CAZE, C. and LOUCHEUX, C. : I.U.P.A.C. Symposium on macromolecular chemistry MAINZ (1979).
TAMIKADO, T. : J. Polym. Sci. 43, 489 (1960).

Received November 13, 1980
Accepted November 18, 1980