Phase-transfer catalysis in the chemical modification of polymers: 1.

Thanh Dung N'Guyen, Alain Deffieux and Sylvie Boileau
Laboratoire de Chimie Macromoléculaire associé au CNRS, Université Pierre et Marie Curie, T. 44, 4 Place Jussieu, 75230 Paris Cédex 05, France
(Received 27 September 1977; revised 7 November 1977)

Phase-transfer catalysts have been successfully employed for the reaction of amines and alcohols with chloromethylated polymers and copolymers. Influence of solvent, catalyst and of reaction time has been studied. The nature of the amine as well as that of the polymeric substrate has been varied. This simple process of chemical modification has led to 100% conversions of chloromethyl groups in some cases.

INTRODUCTION

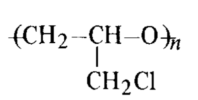
Since the investigations of Jarousse[1] and Makosza[2], phase-transfer catalysis has been widely used in organic chemistry[3,4] particularly for alkylations of alcohols[5–9] and of amines[10–20]. Generally the reaction is conducted by stirring two liquid phases: an organic substrate and 50% aqueous sodium hydroxide with a quaternary ammonium or phosphonium salt as a catalyst. On the other hand, it has been shown that crown ethers, cryptands and poly(ethylene glycol) derivatives are at least as useful as onium salts in phase-transfer catalysed reactions such as nucleophilic displacements, alkylations of carbanions, oxidations and reductions[21–24].

Owing to its simplicity and the low cost of the reagents (in the case of quaternary ammonium salts) phase-transfer catalysis will soon find universal application and will be extended to more and more types of reaction. However, this method has received surprisingly very little attention in the field of the chemical modification of polymers. Roovers[25] has adapted a process using crown ethers to solubilize and activate potassium acetate in non-polar solvents to the acetylation of partly chloromethylated polystyrene.

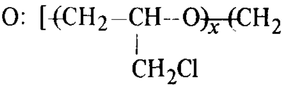
We have prepared several polymers containing pendant amine groups by reaction of amines with chloromethylated polymers and copolymers, using phase-transfer catalysis conditions. Influence of solvent, catalyst and reaction time has been studied. The nature of the amine as well as that of the polymeric substrate has been varied. The results of this investigation are presented in this first paper.

EXPERIMENTAL

Amines and alcohol as well as solvents (nitrobenzene, benzene, tetrahydrofuran, chloroform, methyl ethyl ketone and dimethylformamide) were pure grade commercial products and were used without further purification. Chloromethylated polymers were also commercial samples: polyepichlorhydrin (HERCLOR H from Hercules Co.) (designated PECH); a random copolymer of epichlorhydrin and ethylene oxide (HERCLOR C from Hercules Co.) (PECH–EO); a soluble partly chloromethylated polystyrene (Dow Chemical Co.) (PCMS) and a Merrifield polymer (Fluka) (PM). They were purified by dissolution or swelling in chloroform and precipitation in methanol twice before drying under high vacuum. Composition of these polymers was determined by elemental analysis:

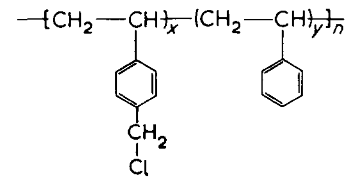
PECH: 
$$-(CH_2-\underset{CH_2Cl}{CH}-O)_n$$

C, 39.1%; H, 5.6%; Cl, 36.8%; O, 18.3%. Theoretical values: C, 38.9%; H, 5.4%; Cl, 38.0%; 0, 17.4%.

PECH–EO: 
$$[(CH_2-\underset{CH_2Cl}{CH}-O)_x(CH_2-CH_2)_y]_n$$

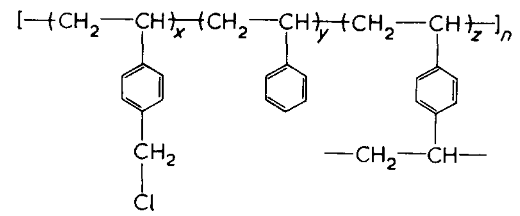
Found: C, 42.4%; H, 6.4%; Cl, 29.3%; O, 22.0% which corresponds nearly to $x = 3$ and $y = 2$.

PCMS:



C, 82.8%; H, 7.5%; Cl, 10.6% which corresponds nearly to $x = 3$ and $y = 7$.

PM:



C, 75.9%; H, 6.4%; Cl, 17.7% which corresponds nearly to $x = 25$, $y = 10$ and $z = 1$. (Crosslinked polymer modified in swollen state).

Phase-transfer catalysts were tetrabutylammonium hy-

Table 1 Influence of the solvent on the reaction of carbazole with poly(epichlorhydrin) homopolymer (PECH) and copolymer (PECH–EO) at 60°C. (Catalyst: TBAH, 5 mol % of the chlorine content of polymer)

Chloro-methylated polymers	Solvents	Reaction times (h)	Degree of substitution
PECH	Chloroform	3	0
PECH	Nitrobenzene	4	~2
PECH	Methyl ethyl ketone	6	4
PECH	Dimethylformamide	3	31
PECH–EO	Benzene	4	3
PECH–EO	Benzene–DMF (50/50)	6	11
PECH–EO	DMF	3	31

drogensulphate (TBAH) (Fluka), dicyclohexyl-18-crown-6 (DCHE) (Aldrich) and Kryptofix [222] (Merck). Typically, 15 mmol of amine or alcohol and 0.5 mmol (or more in some cases) of catalyst were added to a biphasic mixture of a 150 ml polymer solution, containing 10 mmol of chlorine, and 4 ml of a 50% aqueous sodium hydroxide solution. The mixture was magnetically stirred at 60°C for a given time, then filtered after cooling (except in the case where the polymer is insoluble). The polymer was recovered after precipitation in methanol and purified by several dissolutions or swellings in chloroform followed by precipitations in methanol and in hexane. It was dried under high vacuum.

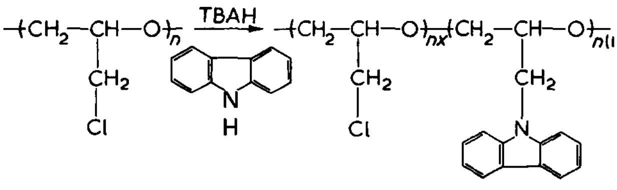
Analysis of the modified polymers were made by infrared, proton n.m.r. and, eventually, u.v. spectrophotometry. The percentage of *N*- or *O*-alkylation was determined by elemental microanalysis from the percentages of N and Cl remaining. Under the chosen experimental conditions the substitution reaction alone occurs. Elimination reactions would lead to the formation of double bonds in the polymers. Occurrence of such linkages in the modified polymers was not detected in i.r. and n.m.r. spectra.

G.p.c. analysis of polymers shows a decrease of the molecular weights after the modification with carbazole, namely for epichlorhydrin polymers and copolymers. For instance the average molecular weight of PECH is reduced by a factor of 10 (with 30% TBAH, in DMF, after 4.5 h at 60°C; see *Table 2*) whereas it is shortened by a factor of 4 for PCMS (with 5% TBAH, in DMF, after 2 h at 60°C; see *Table 2*).

RESULTS AND DISCUSSION

Influence of the solvent

The solvent used must allow the extraction of the aqueous phase of the active ionic species ($R_4N^+A^-$) and favour the alkylation reaction at the expense of side reactions (elimination, polymer degradation . . .). Different solvents were tried in the case of the reaction of carbazole with polyepichlorhydrin polymers and copolymers using TBAH as a catalyst. Results are given in *Table 1*. Chloromethyl group conversions were determined by elemental analysis of N and Cl percentages in the polymer. We carried out spectrophotometric titration at 343 nm of the substituted carbazyl groups in THF polymer solutions:



The ultra-violet spectrum of substituted polymers is essentially identical with that of *N*-ethylcarbazole for which ϵ_{max} (346 nm) = 4170[26]. Agreement between both methods of analysis is quite good for low percentages of substitution. However some discrepancies appear for higher carbazole contents in polymers as can be seen in *Table 3*. As noticed by Gibson *et al.*[27] for poly(vinylbenzyl chloride) polymers modified by carbazyl anions, some sort of interaction between adjacent chromophores is involved thus leading to a dependence of ϵ on the molar carbazole content of the polymer and showing that u.v. spectrophotometry is not a dependable method for an estimation of the composition of such polymers.

From the results of *Table 1*, it can be seen that DMF is the most convenient solvent, thus it has been used for all the other experiments.

Influence of the catalyst

We have compared the efficiency of a quaternary ammonium salt (TBAH) to that of a crown ether (DCHE) and of a cryptand [222]. Moreover, the influence of the catalyst concentration has been examined in the case of the onium salt. The results are summarized in *Table 2*. For a given catalyst concentration, the efficiency follows the decreasing order: [222] > DCHE > SO_4HNBu_4. However, even with the quaternary ammonium salt, rather large yields of chloromethyl group conversion are obtained. A slight increase of the carbazole content in the polymer is observed on increasing the catalyst concentration. A 5% molar concentration relative to the chlorine content of polymer appears to give satisfactory yields of grafted carbazole.

Influence of the reaction times

Progress of the substitution reaction of chlorine in different polymers with carbazole is shown in *Figure 1* and in *Table 3*. With polymers derived from epichlorhydrin (PECH and PECH–EO) the substitution reaches more or less rapidly a plateau, the value of which depends on the solvent and on catalyst concentration. The fact that it is not possible to obtain a 100% conversion of chloromethylated groups might be due to steric hindrance of carbazyl substituents which does not occur for partly chloromethylated polystyrene.

Influence of the substituent and of the polymer

We have compared the reactivities of different amines and of an alcohol with a given chloromethylated polymer

Table 2 Influence of the catalyst on the reaction of carbazole with chloromethylated polymers in DMF at 60°C

Chloro-methylated polymers	Catalysts	Concen-trations[a] (%)	Reaction times (h)	Degree of substitu-tion (%)
PECH	None	0	24.0	<1
PECH	TBAH	5	5.0	41
PECH	TBAH	30	4.5	52
PECH	TBAH	100	5.0	56
PECH	DCHE	5	5.0	52
PECH	[222]	5	5.0	66
PECH–EO	TBAH	5	5.0	32
PECH–EO	TBAH	30	4.5	41
PCMS	None	0	18.0	<1
PCMS	TBAH	5	2.0	98

[a] Molar percentage of the chlorine content of polymer

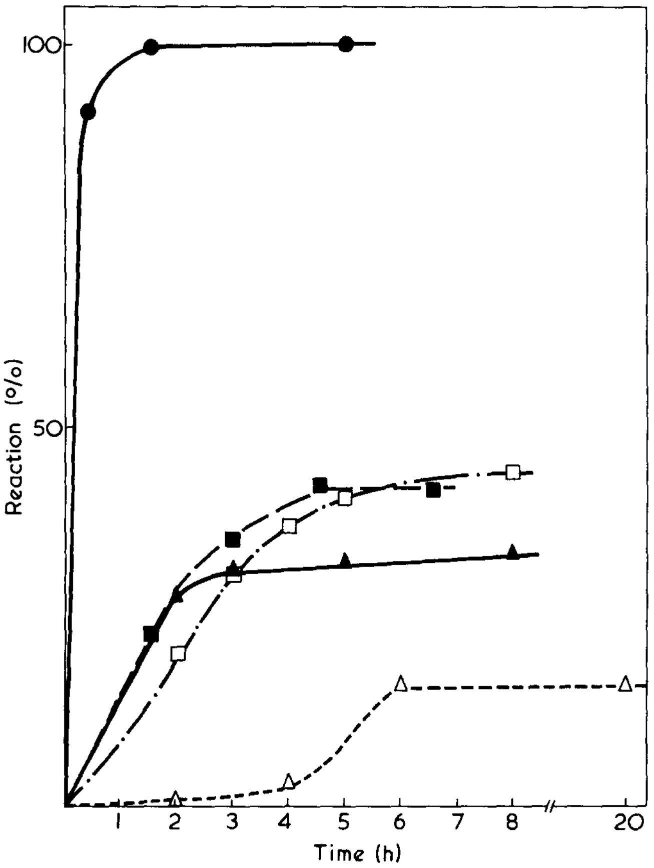


Figure 1 Progress of the substitution reaction of chlorine in partly chloromethylated polymers: ●, PM 5% TBAH in DMF; □, PECH 5% TBAH in DMF; ▲, PECH–EO 5% TBAH in DMF; ■, PECH–EO 30% TBAH in DMF; △, PECH–EO 5% TBAH in benzene

Table 3 Influence of the reaction times on the reaction of carbazole with polyepichlorhydrin copolymer (PECH–EO) in DMF at 60°C. Catalyst: TBAH, 5 mol % of the chlorine content of polymer

Reaction times (h)	Degree of substitution (%) (a)	 (b)
2	28	28
3	31	31
5	32	32
8	33	39

(a) Determined by elemental analysis; (b) determined by u.v. spectrophotometric titration at 343 nm

together with the reactivities of different polymers with a given amine. The results are summarized in *Table 4*. In the case of epichlorhydrin polymer and copolymer, the best substitution yields are obtained with compounds having the most acidic hydrogen, that is, for carbazole and 2,3-dimethylindole. In similar conditions aliphatic amines give low degrees of substitution. *Para*-chloromethylstyrene polymers are more reactive than the other chloromethylated polymers. Yields of substitution are higher after shorter times of reaction and even aliphatic amines lead to high levels of conversion. It can be seen that a crosslinked polymer such as the Merrifield resin is completely substituted by carbazole after 2.5 h of reaction. This is due to the fact that chlorine is more labile in poly(*para*-chloromethylstyrene) than in epichlorhydrin.

Table 4 Influence of the nature of the substituent and of the polymer on the reaction of amines and alcohol with chloromethylated polymers at 60°C in DMF. Catalyst: TBAH, 5 mol % of the chlorine content of polymer

Chloromethylated polymers	Substituents	Reaction times (h)	Degree of substitution (%)
PECH	Carbazole	5	41
PECH	2,3-Dimethylindole	4	52
PECH	Dibutylamine	5	5
PECH	Diethylamine	5	9
PECH	Isobutylamine	6	8
PECH	*N,N*-Diethylethanol amine	6	7
PCMS	Carbazole	2	88
PCMS	2,3-Dimethylindole	2	79
PCMS	Dibutylamine	1.5	75
PCMS	*N,N*-Diethylethanol amine	1.5	65
PM	Carbazole	0.5	91
PM	Carbazole	2.5	100

CONCLUSION

We have shown that phase-transfer catalysis can be successfully employed for the reaction of amines with chloromethylated polymers and copolymers. The best solvent found for this type of reaction is DMF. Cryptand and crown ether are more effective than tetrabutylammonium hydrogensulphate as catalysts; however yields of substitution remain quite high with this last compound which is less expensive than the former ones. This simple process leads to the formation of polymers containing pendant amine groups which might present various interesting properties. Very recently Gibson *et al.*[27] have presented a method of synthesis of poly [(*N*-carbazyl)methylstyrene] which requires more complicated steps, particularly the preparation of carbazylpotassium in xylene. Applications of phase-transfer catalysis to other chemical modifications of polymers as well as the studies of modified polymers are in progress.

REFERENCES

1 Jarousse, M. J. *C. R. Acad. Sci. (C) (Paris)* 1951, **232**, 1424
2 Makosza, M. and Serafin, B. *Rocz. Chem.* 1965, **39**, 1223
3 Dockx, J. *Synthesis* 1973, p 441
4 Dehmlow, E. V. *Angew. Chem. Int. Edn Engl.* 1974, **13**, 170; *Chem. Technol.* 1975, p 211
5 Herriott, A. W. and Picker, D. *Tetrahedron Lett.* 1972, p 4521
6 Merz, A. *Angew. Chem. Int. Edn Engl.* 1973, **12**, 846
7 Cazes, B. and Julia, S. *Tetrahedron Lett.* 1974, p 2077
8 Freedman, H. H. and Dubois, R. A. *Tetrahedron Lett.* 1975, p 3251
9 Dehmlov, E. V. and Schmidt, J. *Tetrahedron Lett.* 1976, p 95
10 Berg-Nielsen, K. and Bernatek, E. *Acta Chem. Scand.* 1972, **26**, 4130
11 Jonczyk, A. and Makosza, M. *Rocz. Chem.* 1975, **40**, 1203; *Synthesis* 1976, p 795
12 Brehme, R. *Synthesis* 1976, p 114
13 Barco, A., Benetti, S., Pollini, G. P. and Baraldi, P. G. *Synthesis* 1976, p 124
14 Bocchi, V., Casnati, G., Dossena, A. and Villani, F. *Synthesis* 1976, p 414
15 Palecek, J. and Kuthan, J. *Synthesis* 1976, p 550
16 Dou, H. J. M. and Metzger, J. *Bull. Soc. Chim. Fr.* 1976, p 1861
17 Suvorov, N. N., Smushkevich, Y. I., Velezheva, V. S., Rozhkov, V. S. and Simakov, S. V. *Khim. Geterotsikl. Soedin.* 1976, **2**, 191; *Chem. Abstr.* 1976, **83**, 179957
18 Maurette, M. T., Lopez, A., Martino, R. and Lattes, A. *C. R. Acad. Sci. (Paris)* 1976, **282**, 599
19 Cacchi, S., La Torre, F. and Misiti, D.*Synthesis* 1977, p 301

20 Masse, J. *Synthesis* 1977, p 341

21 Gokel, G. W. and Durst, H. D. *Synthesis* 1976, p 168 and references therein

22 Vögtle, F. and Weber, E. *Kontakte* 1977, **1**, 11 and references therein

23 Cinquini, M., Colonna, S., Molinari, H. and Montanari, F. *J. Chem. Soc. Chem. Commun.* 1976, p 394

24 Lehmkuhl, H., Rabet, F. and Hauschild, K. *Synthesis* 1977, p 184

25 Roovers, J. E. L. *Polymer* 1976, **17**, 1107

26 Boileau, S. and Sigwalt, P. *Bull. Soc. Chim. Fr.* 1968, p1418

27 Gibson, H. W. and Bailey, F. C. *Macromolecules* 1976, **9**, 688