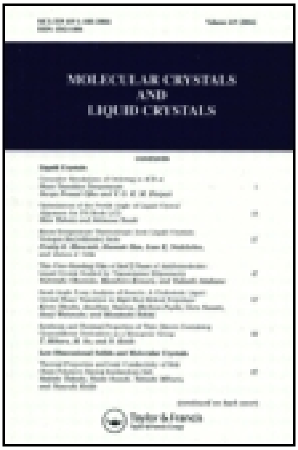


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mixed Quaternary Ammonium and Phosphonium Salts Bound to Macromolecular Supports for Removal Bacteria from Water

A. Popa [a] , G. Ilia [a] , S. Iliescu [a] , G. Dehelean [a] , A. Pascariu [a] , A. Bora [a] & C. M. Davidescu [b]

[a] Institute of Chemistry Timisoara of Romanian Academy, Timisoara, Romania

[b] Physical Chemistry Department, Timisoara, Romania

Version of record first published: 18 Oct 2010

To cite this article: A. Popa, G. Ilia, S. Iliescu, G. Dehelean, A. Pascariu, A. Bora & C. M. Davidescu (2004): Mixed Quaternary Ammonium and Phosphonium Salts Bound to Macromolecular Supports for Removal Bacteria from Water, Molecular Crystals and Liquid Crystals, 418:1, 195-203

To link to this article: http://dx.doi.org/10.1080/15421400490479280

Mol. Cryst. Liq. Cryst., Vol. 418, pp. 195/[923]–203/[931], 2004
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490479280

MIXED QUATERNARY AMMONIUM AND PHOSPHONIUM SALTS BOUND TO MACROMOLECULAR SUPPORTS FOR REMOVAL BACTERIA FROM WATER

A. Popa, G. Ilia, S. Iliescu, G. Dehelean, A. Pascariu, and A. Bora
Institute of Chemistry Timisoara of Romanian Academy,
B-dul Mihai Viteazul 24, 1900 Timisoara, Romania

C. M. Davidescu
Industrial Chemistry and Environment Engineering Faculty,
Physical Chemistry Department, B-dul V. Parvan 6,
1900 Timisoara, Romania

This paper deals with synthesis and characterization of mixed quaternary ammonium and phosphonium salts grafted on macromolecular supports by polymer-analogous trans-quaternization reactions. The degrees of functionalization with quaternary mixed ammonium and phosphonium groups are relatively high, ranging from 0.09 to 1.285 mmoles of functional groups/gram of copolymer, ensuring a sufficient concentration of active centers per unit mass of copolymer and being well suited for application as antibacterial agents.

Keywords: mixed quaternary ammonium and phosphonium salts; polymer-analogous trans-quaternization reaction

INTRODUCTION

Polymer-supported reagents are important in catalysis [1,2], organic synthesis [3], trace analysis and environmental separations [4,5]. Polystyrene has been used most often as the support for phase transfer catalysts mainly because of the availability of Merrifield resins [6] and quaternary ammonium ion exchange resins [7]. Recently, their antibacterial activity was also reported [8–10].

Address correspondence to A. Popa, Institute of Chemistry Timisoara of Romanian Academy, B-dul Mihai Viteazul 24, Timisoara, 1900, Romania. E-mail: apopa@acad-tim.utt.ro

In the current research, we describe the results obtained in the synthesis of the mixed quaternary ammonium and phosphonium salts grafted on macromolecular supports by polymer-analogous trans-quaternization reactions using as precursors polymeric quaternary ammonium salts.

Our purpose was to obtained products to be used as polymeric biocides, where the presence of mixed onium groups would introduce synergistic effects on antibacterial activity [11].

EXPERIMENTAL

Reagents

The following reagents were used: triethylphosphine (Aldrich, 99%), triphenylphosphine (Merck, p.a.), N,N-dimethylformamide (Carlo Erba, p.a.), acetone (Chimopar Romania, p.a.), chloroform (Chimopar Romania, p.a.), ethyl ether (Chimopar Romania, p.a.) and quaternary ammonium salts grafted on macromolecular supports used as starting materials are presented in Table 1.

Synthesis of the Functionalized Copolymer by Polymer-analogous Trans-quaternization Reaction

In a 250 ml round-bottom flask fitted with reflux condenser, mechanical stirrer, thermometer and previously purged with nitrogen, 10 grame of copolymer functionalized with quaternary ammonium salts and 150 ml of N,N-dimethylformamide were added. The mixture was then maintained

TABLE 1 Properties of the Quaternary Ammonium Salts Grafted on Styrene-7% divinylbenzene used as Source Copolymers

							Mmoles/grame of copolymer	
Code	R_{3-n}	R'_n	Cl (%,W)	N (%,W)	$x - y$[a]	y[b]	$N^+R_{3-n}R'_n$	$-CH_2Cl$
A1	$(C_4H_9)_3$	–	12.54	1.06	0.520	0.120	0.75	3.26
A2	$(C_6H_{13})_3$	–	7.94	1.62	0.410	0.230	1.16	2.06
A3	$(C_8H_{17})_3$	–	5.74	1.77	0.350	0.290	1.24	1.47
A4	$C_{13}H_{27}$	$(C_2H_4OH)_2$	11.28	1.04	0.518	0.129	0.84	3.36
A5	C_6H_5	$(CH_3)_2$	4.18	3.24	0.200	0.440	2.30	1.57
A6	C_6H_5	$(C_2H_5)_2$	12.75	1.15	0.519	0.128	0.82	3.33
A7	$(C_6H_5CH_2)_2$	–	14.50	0.57	0.584	0.063	0.43	4.02

[a] Fraction of styrene units functionalized with chloromethyl groups.

[b] Fraction of styrene units functionalized with quaternary ammonium groups.

under stirring for 2 hours at room temperature for swelling the copolymer beads. We used a molar ratio of quaternary ammonium groups to phosphine of 1:1.5. The necessary amount of triethylphosphine or triphenylphosphine dissolved in N,N-dimethylformamide was added dropwise in 15 minutes. Nitrogen atmosphere was maintained throughout the reaction time of 24 hours at the temperature of 110°C. After cooling, the polymer beads were separated by filtration, washed with chloroform (3 × 20 ml), acetone (3 × 20 ml) and ethyl ether (3 × 20 ml), and dried under a vacuum of 2 kPa at 50°C for 24 hours.

Determination of the Phosphorus Content

A sample of the final products precisely weighted was burnt out in an oxygen atmosphere and the P_2O_5 formed was absorbed in water. The solution obtained was titrated with an aqueous solution of cerium (III) 0.005 M in the presence of Eryochrome Black T as indicator.

Determination of the Nitrogen Content

A sample of the final reaction product, precisely weighted, was disintegrated with concentrated sulphuric acid. The nitrogen absorbed in an aqueous solution as $(NH_4)_2SO_4$ was freed as NH_3 with a concentrated aqueous NaOH solution and then collected in a concentrated aqueous HCl solution with known titre. The excess of concentrated aqueous HCl was then back titrated with an aqueous NaOH solution with known titre.

Determination of the Chlorine Content

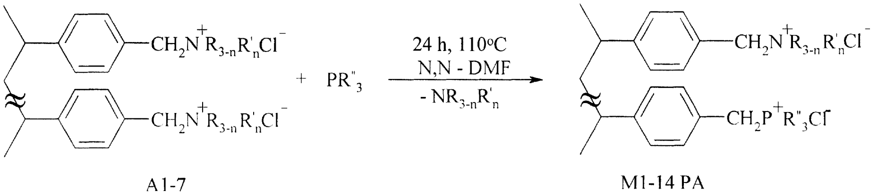
A sample of the final reaction product, precisely weighted, was burnt out in an oxygen atmosphere, the gases were absorbed in an aqueous solution of H_2O_2 0.15% (W) and the chloride ion was quantitatively determined by potentiometric titration with an aqueous solution of $AgNO_3$ 0.05 M.

RESULTS AND DISCUSSION

The polymer-analogous trans-quaternization reaction is presented in Scheme 1.

Characterization of Mixed Quaternary Onium Salts

The products are clearly confirmed as mixed quaternary ammonium and phosphonium salts by the following observations resulted from the analysis of the IR spectra:



where: n = 0; 2.

R = alkyl or phenyl

R' = alkyl

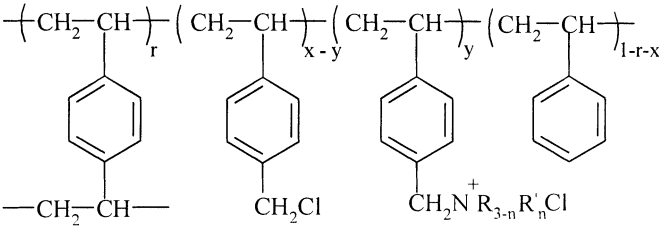
R'' = ethyl or phenyl

SCHEME 1 Preparation of polymer-grafted mixed onium salts by trans-quaternization of a styrene-7% divinylbenzene copolymer functionalized with quaternary ammonium groups.

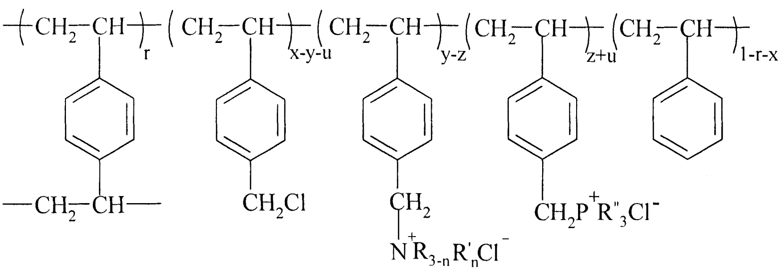
- a strong decrease of the intensity of the absorption bands at: 2950–2970, 2916–2936; 2860–2882, 2843–2863; 1450–1475, 1377–1383 cm^{-1} due respectively to $\nu^{as}CH_3$, $\nu^{as}CH_2$; $\nu^{s}CH_3$, $\nu^{s}CH_2$; $\delta^{as}CH_3$, CH_2 and $\delta^{s}CH_3$ was pointing out that the trans-quaternization reaction took place, as expected at the $-N^+R_{3-n}R'_nCl^-$ groups.
- The decrease in the intensity of the chloromethyl absorption bands νCH_2Cl and δCH_2Cl at 1260 cm^{-1} and 1430 cm^{-1} was suggesting that a direct quaternization of the residual chloromethyl groups of the initial copolymer also took place, along with the main reaction of trans-quaternization of the quaternary ammonium groups. As quaternary phosphonium groups were formed, this side reaction of direct quaternization was a useful one, increasing the overall yield of reaction.
- The formation of the quaternary phosphonium groups $-P^+Ph_3Cl^-$ was confirmed by the appearance of the absorption bands at 1440–1430 and 1120–1100 cm^{-1} associated with the vibrations of the $P-C_{phenyl}$ and $C_{phenyl}-H$ bonds.

Determination of the Functionalization Degrees and the Yields of Formation of the $-P^+R''_3Cl^-$ groups

The fraction of the repetitive unit functionalized with quaternary ammonium and respectively phosphonium groups was determined based on the content of nitrogen, phosphorus and chlorine in the final copolymer and by accepting the statistical structure of the repetitive unit of the initial and final copolymer presented in Figure 1.



Repetitive unit of the initial copolymer



Repetitive unit of the final copolymer

FIGURE 1 Statistical structure of the repetitive unit of the copolymers.

USING THE NOTATIONS:

x – fraction of styrene units bearing pendant $-CH_2Cl$ groups

y-z – fraction of styrene units bearing pendant $-N^+R_{3-n}R'_nCl^-$, (n = 0,2) groups

z – fraction of styrene units bearing pendant $-P^+R''_3Cl^-$ groups obtained by polymer-analogous trans-quaternization

u – fraction of styrene units bearing pendant $-P^+R''_3Cl^-$ groups obtained by polymer-analogous quaternization

r – fraction of divinylbenzene type units

Mmf – average molecular weight of the repetitive unit of the final copolymer

%N – nitrogen percentage in the final copolymer

%P – phosphorus percentage in the final copolymer

%Cl – chlorine percentage in the final copolymer

A_{Cl} – atomic weight of chlorine

A_N – atomic weight of nitrogen

A_P – atomic weight of phosphorus

G_F – degree of functionalization of the final copolymer
η_F – yield of the polymer-analogous reaction

The fraction of the styrene units bearing pendant $-P^+R''_3Cl^-$ groups, obtained by polymer-analogous trans-quaternization and respectively quaternization were calculated with the Eqs. (1–3):

$$Mmf = \frac{x \cdot A_{Cl}}{\%Cl} \times 100 \tag{1}$$

$$z = y - \%N \times \frac{M_{mf}}{100 \cdot A_N} \tag{2}$$

$$u = \%P \times \frac{M_{mf}}{100 \cdot A_P} - z \tag{3}$$

On this basis, the degrees of functionalization with $-P^+R''_3Cl^-$ groups and residual $-N^+R_{3-n}R'_nCl^-$ and $-CH_2Cl$ groups were calculated respectively with Eqs. (4–6):

$$G_{F1} = (z + u)/M_{mf} \ (\text{mmoles of} - \mathrm{P^+R_3''Cl^-} \ \text{groups/g. of copolymer}) \tag{4}$$

$$G_{F2} = (y - z)/M_{mf} \ (\text{mmoles of} \ - \mathrm{N^+R_{3-n}}R'_{\mathrm{n}}\mathrm{Cl^-}/\text{g. of copolymer}) \tag{5}$$

$$G_{F3} = (x - y - u)/M_{mf} \ (\text{mmoles of} - \mathrm{CH_2Cl} \ \text{groups/g. of copolymer}) \tag{6}$$

The yields of the polymer-analogous trans-quaternization reaction were calculated with the Eqs. (7,8):

$$\eta_{F1} = z/y \cdot 100 \ (\text{molar\%}) \tag{7}$$

$$\eta_{F2} = u/(x - y) \cdot 100 \ (\text{molar\%}) \tag{8}$$

The main characteristics of the supported products prepared by polymer-analogous trans-quaternization reactions are given in Tables 2, 3:

The trans-quaternization reaction consist in the attack of the tertiary phosphine to the ammonium salt followed by the transfer of the intermediary formed radical and the onium function from nitrogen to phosphorus.

The increase in the alkyl chain length of the ammonium groups had an unfavorable effect, the best activities being obtained with tributhylammonium derivatives (see Fig. 2.).

The phosphonium functionalization degrees of mixed salts with triethylphosphonium were, in most cases lower.

A very good phosphonium functionalization degree was proved to be mixed product M11PA, with triphenylphosphonium and with the ammonium

TABLE 2 Characteristics of the Mixed Ammonium and Phosphonium Salts Grafted on Polymeric Support

No.	Code	R''	R_{3-n}	R'_n	Cli (%,W)	Clf (%,W)	Ni (%,W)	Nf (%,W)	P (%,W)
1	M1PA	C_2H_5	$(C_4H_9)_3$	–	12.54	7.36	1.06	0.39	1.17
2	M2PA	C_2H_5	$(C_6H_{13})_3$	–	7.94	5.69	1.62	0.58	1.02
3	M3PA	C_2H_5	$(C_8H_{17})_3$	–	5.74	4.61	1.77	0.73	0.92
4	M4PA	C_2H_5	$C_{13}H_{27}$	$(C_2H_4OH)_2$	11.28	7.65	1.04	0.57	1.39
5	M5PA	C_2H_5	C_6H_5	$(CH_3)_2$	4.18	4.03	3.24	0.89	1.21
6	M6PA	C_2H_5	C_6H_5	$(C_2H_5)_2$	12.75	10.39	1.15	0.67	0.89
7	M7PA	C_2H_5	$(C_6H_5CH_2)_2$	–	14.50	11.68	0.57	0.29	0.98
8	M8PA	C_6H_5	$(C_4H_9)_3$	–	12.54	5.42	1.06	0.13	1.69
9	M9PA	C_6H_5	$(C_6H_{13})_3$	–	7.94	4.75	1.62	0.37	1.58
10	M10PA	C_6H_5	$(C_8H_{17})_3$	–	5.74	4.39	1.77	0.38	1.39
11	M11PA	C_6H_5	$C_{13}H_{27}$	$(C_2H_4OH)_2$	11.28	7.68	1.04	0.47	4.01
12	M12PA	C_6H_5	C_6H_5	$(CH_3)_2$	4.18	4.09	3.24	0.51	2.15
13	M13PA	C_6H_5	C_6H_5	$(C_2H_5)_2$	12.75	9.98	1.15	0.59	2.13
14	M14PA	C_6H_5	$(C_6H_5CH_2)_2$	–	14.50	9.81	0.57	0.31	1.67

ion having 2-hidroxyethyl groups associated with long chain (C13) alkyl substituents.

The presence of aril radicals in the environment of phosphonium salts had an unfavorable effect both the functional degrees and yields.

TABLE 3 Characteristics of the Final Copolymers Obtained by Polymer-analogous Trans-quaternization Reaction

					Mmoles/g. of copolymers				
Code	$x-y-u$	$y-u$	z	u	Mmf	N^+	P^+	CH_2Cl	η_{F1} (%)	η_{F2} (%)
M1PA	0.474	0.050	0.070	0.046	308.35	0.162	0.376	1.537	58.33	8.84
M2PA	0.350	0.160	0.070	0.060	398.85	0.401	0.326	0.877	30.43	14.63
M3PA	0.250	0.250	0.040	0.100	492.28	0.507	0.284	0.507	13.79	28.57
M4PA	0.390	0.121	0.009	0.120	296.65	0.407	0.434	1.314	6.92	23.53
M5PA	0.060	0.360	0.080	0.140	563.14	0.439	0.390	0.106	18.18	70.00
M6PA	0.473	0.105	0.015	0.047	218.43	0.480	0.284	2.165	12.50	9.03
M7PA	0.540	0.080	0.020	0.040	194.30	0.205	0.308	0.277	33.33	6.89
M8PA	0.374	0.038	0.082	0.146	418.72	0.090	0.544	0.893	68.33	28.07
M9PA	0.270	0.130	0.100	0.140	477.64	0.272	0.502	0.565	43.47	34.15
M10PA	0.260	0.150	0.140	0.090	516.81	0.290	0.445	0.503	48.27	25.71
M11PA	0.160	0.100	0.030	0.350	295.50	0.338	1.285	0.541	23.07	68.63
M12PA	0.050	0.210	0.230	0.150	554.87	0.378	0.685	0.090	52.27	75
M13PA	0.386	0.098	0.030	0.126	227.39	0.430	0.686	1.697	23.44	24.61
M14PA	0.470	0.050	0.010	0.110	231.33	0.216	0.518	2.030	16.66	18.96

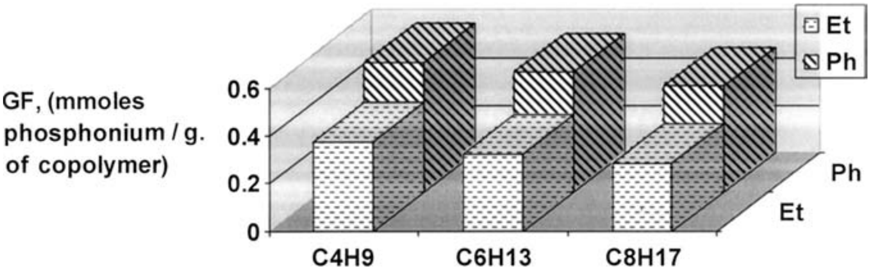


FIGURE 2 Effect of number of carbon atoms in the alkyl radicals of the ammonium ion on the phosphonium functionalization degrees.

In ammonium salts the influence of aril radicals had a favorable effect both the functional degrees and yields (see Table 3).

CONCLUSIONS

The proposed procedures for the synthesis of mixed quaternary phosphonium and ammonium salts grafted on crosslinked polymer-supports by trans-quaternization of the quaternary ammonium salts grafted on macromolecular supports are simple and efficient.

The trans-quaternization reaction takes place simultaneously with a benefic side reaction of direct quaternization of the residual chloromethyl groups of the copolymer by the phosphine reagents.

The products obtained have all the needed characteristics which enable this uses as phase transfer catalysts, intermediates for obtaining other functionalized copolymers by polymer-analogous reactions, or as policationic biocides, interesting synergistic effects on the antibacterial activity are to be expected due to presence of mixed quaternary phosphonium and ammonium pendant groups.

REFERENCES

[1] Tomoi, M. & Ford, W. T. (1988). Polymeric phase transfer catalysts. In: *Syntheses and Separations using Functional Polymers*, Sherrington, D. C. & Hodge, P. (Eds.), John Wiley & Sons: New York, 181–207.

[2] Sherrington, D. C. (1980). Catalysis by ion-exchange resins and related materials. In: *Polymer-Supported Reactions in Organic Synthesis*, Hodge, P. & Sherrington, D. C. (Eds.), John Wiley & Sons: New York, 157–194.

[3] Hodge, P. (1980). Polymer-supported reagents. In: *Polymer-Supported Reactions in Organic Synthesis*, Hodge, P. & Sherrington, D C. (Eds.), John Wiley & Sons: New York, 83–155.

[4] Alexandratos, S. D. & Crick, D. W. (1996). Polymer-supported reagents: Application to separation science. *Ind. Eng. Chem. Res.*, *35*, 635–644.

[5] Beauvais, R. A. & Alexandratos, S. D. (1998). Polymer-supported reagents for the selective complexation of metal ions: an overview. *Reactive & Functional Polymers*, *36*, 113–123.

[6] Merrifield, R. B. (1963). Solid phase peptide synthesis I. The synthesis of a tetrapeptide. *JACS*, *85*, 2149–2154.

[7] Warth, L. M., Cooper, R. S., & Fritz, J. S. (1989). Low-capacity quaternary phosphonium resins for anion chromatography. *J. of Chromatography*, *479*, 401–409.

[8] Ikeda, T. & Tazuke S. (1984). Biologically active polycations, 4) Synthesis and antimicrobial activity of poly(Trialkylvinylbenzylammonium chloride)s. *Makromol. Chem.*, *185*, 869–876.

[9] Kanazawa, A., Ikeda, T., & Endo, T. (1993). Novel polycationic biocides: Synthesis and antibacterial activity of polimeric phosphonium salts. *J. of Polymer Science: Part A: Polymer Chemistry*, *31*, 335–343.

[10] Kanazawa, A., Ikeda, T., & Endo, T. (1993). Polymeric phosphonium salts as a novel class of cationic biocides. II. Effects of counter anion and molecular weight on antibacterial activity of polymeric phosphonium salts. *J. of Polymer Science: Part A: Polymer Chemistry*, *31*, 1441–1447.

[11] Kanazawa, A., Ikeda, T., & Endo, T. (1994). Polymeric phosphonium salts as a novel class of cationic biocides. VIII. Synergistic effect on antibacterial activity of polymeric phosphonium and ammonium salts. *J. of Applied Polymer Science*, *53*, 1245–1249.