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BINDING OF POLYMER MOLECULES WITH TERTIARY AMINE GROUPS BY HALOGEN-CONTAINING COMPOUNDS

M. BEZDĚK, V. HYNKOVÁ, K. BOUCHAL and F. HRABÁK

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6—Petřiny, Czechoslovakia

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Abstract—Soluble polymers and copolymers with bound tertiary amine groups react at room temperature with halogens and halogen compounds to give crosslinked systems. Crosslinking occurs in solution, emulsion and in polymer mixtures, in ultra-violet and visible light and in the dark.

PREVIOUS work[1] has shown that unstable esters of α-amino alcohols $R^1R^2NCH(R^3)$-$OCOR^4$ and α-halogeno-amines $R^1R^2NCH(R^3)$hal condense with tertiary amines to give oligomeric amines. Later, in an investigation of the condensation reactions of esters of α-aminocarbinols,[2] gel-chromatographic analysis confirmed qualitatively[3] the formation of oligomeric amines during the reaction of N,N-dimethylaniline and N-N-dimethyl-*p*-toluidine with tetrachloromethane.

The results of subsequent work[4] showed that soluble polymers and copolymers with bound tertiary amino groups can be crosslinked at normal temperature by reaction with halogens or halogen compounds. This process of binding the macromolecules has been proved in solution, emulsion and in polymer mixtures; it can be accelerated by a simultaneous action of ultra-violet or visible light. The times needed for gel formation after the mixing of amino polymers with a halogen or a halogen compound at room temperature are given in Tables 1–4.

The following polymers containing tertiary amino groups were used: poly(*p*-dimethylaminostyrene), $\bar{M}_n \approx 2{\cdot}4 \times 10^5$ (polyDMAS); poly(2-dimethyl aminoethyl acrylate), $\bar{M}_n > 1{\cdot}0 \times 10^5$ (polyDMAEA); poly(2-dimethylaminoethyl methacrylate), $\bar{M}_n > 1{\cdot}10 \times 10^5$ (polyDMAEMA); copolymer of styrene and *p*-dimethylaminostyrene (polyS + DMAS) (3:1, w/w); copolymer of 2-dimethylaminoethyl acrylate and methyl methacrylate (polyDMAEA + MMA) (1:1, w/w); poly(N-vinylcarbazol) (polyVCZ).

A number of organic and inorganic low-molecular weight compounds (Tables 1–3) and the following halogen-containing polymers and copolymers prepared in our laboratory (Table 4) were used as halogen compounds: poly(2,2,2-trichloroethyl acrylate), $\bar{M}_n \approx 3{\cdot}3 \times 10^5$; poly(1,2,2,2-tetrachloroethyl methacrylate), $\bar{M}_n \approx 4{\cdot}8 \times 10^5$; poly(styrene-co-2,2,2-trichloroethyl acrylate); poly(styrene-co-1,2,2,2-tetrachloroethyl methacrylate); poly(styrene-co-2,3-dichloropropene); poly(styrene-co-trichloroethylene); poly(styrene-co-vinylidene chloride); poly(vinyl chloride), $\bar{M}_n \approx 4{\cdot}6 \times 10^4$; and brominated polychloroprene, $\bar{M}_n > 1{\cdot}0 \times 10^5$ and n_D^{25} 1·585.

TABLE 1. TIME NEEDED FOR GEL FORMATION IN LIGHT AND IN THE DARK AFTER ADDITION OF A HALOGEN COMPOUND (X) TO A SOLUTION OF 0·1 g OF A POLYMER OR A COPOLYMER WITH TERTIARY AMINO GROUPS IN 2 cm^3 OF BENZENE; THE AMOUNT OF X WAS EQUIVALENT TO THE CONTENT OF THE AMINO GROUP IN SOLUTION; ROOM TEMPERATURE; TIMES NEEDED FOR EXPERIMENTS IN THE DARK ARE GIVEN IN BRACKETS. DMAS = *p*-DIMETHYLAMINOSTYRENE, DMAEA = 2-DIMETHYLAMINO ETHYL ACRYLATE, DMAEMA = 2-DIMETHYLAMINOETHYL METHACRYLATE, MMA = METHYL METHACRYLATE, VCZ = N-VINYLCARBAZOLE

Sample no.	X	Gelation time				
		PolyDMAS	PolyDMAEA	PolyDMAEMA	PolyVCZ	Poly(DMAEA + MMA)
1–6	Fluorine	1 min (5 min)		1 min (1 min)		10 min (30 min)*
7	Chlorine		(1 min)			
8	Bromine		(1 min)			
9	Iodine		(1 min)			
10–12	Chloroform	2 hr (36 hr)			1 hr	
13–16	Bromoform	3 hr	3 hr	1 hr		5 hr
17–24	Iodoform	1 hr	5 hr (5 hr)	30 min (30 min)	1 hr	30 min (30 min)
25	Ethyl iodide					(2 hr)
26–27	Trichloroethylene	2 hr (16 hr)				
28–35	Chloral	1 min (5 hr)	1 min (2 min)	1 min (2 min)		1 min (2 min)
36–38	2,2,2-Trichloroethanol	1 hr (6 hr)			1 day	
39–44	Tetrachloromethane	30 min (7 days)	14 days	2 days	4 hr	3 days
45–52	Trichlorobromomethane	1 min (3 hr)	3 hr (3 days)	1 hr (3 days)		3 hr (5 days)
53–60	Tetrabromomethane	3 hr (2 days)	3 hr (2 days)	1 hr (2 days)		1 hr (2 days)
61	2,2,3,3-Tetrafluoropropanol	5 hr				
62–64	1,2,3,4-Tetrachlorobutane	2 hr (14 days)		14 days		
65–69	Hexachloroethane	30 min (10 days)	14 days	2 days		3 days
70–71	Hexachlorocyclohexane	3 hr (16 hr)				
72	Benzyl chloride					(5 hr)
73–74	Toluyl chloride	10 min (30 min)				
75	Phthaloyl chloride†	30 min				
76	Benzenesulphochloride	(1 day)				
77	Thionylchloride	(1 min)				
78	Carbon disulphide	(1 day)				
79	Sulphur monochloride	(1 day)				
80	Phosphoroxychloride					(1 min)
81	Aluminium chloride					(1 min)
82	Ferric chloride‡		(1 min)			
83	Silicon tetrachloride					(1 min)
84	Tin tetrachloride					(1 min)
85–86	Titanium tetrachloride	(1 min)				(1 min)

* In aqueous solution.

† Gel is formed also after addition of organic acid anhydrides, e.g. in the case of phthalic anhydride with PolyDMAS within 2 days.

‡ In ethanol solution.

TABLE 2. TIME NEEDED FOR GEL FORMATION AFTER ADDITION OF A HALOGEN COMPOUND (X = $3 \cdot 5 \times 10^{-4}$ mol) TO A SOLUTION OF 0·1 g OF POLY(2-DIMETHYLAMINOETHYL ACRYLATE) IN 2 cm^3 WATER AT ROOM TEMPERATURE IN THE DARK

Sample no.	X	Gelation time
87	Chloral	(1 min)
88	Cobalt dichloride	(4 days)
89	Rhodium trichloride	(1 min)
90	Titanium tetrachloride	(6 days)
91	Potassium bromide	(6 days)
92	Potassium iodide	(6 days)

The polymer and copolymer solutions in an organic solvent (Table 1) or in water (Table 2), or aqueous emulsions of polymers (Table 3) were irradiated with a mercury discharge tube in Sial glass ampoules (Czechoslovakia) closed with a tap, for up to 6 hr. If no gel formation occurred within this time, the ampoule was stored at room temperature with alternating daylight (scattered light filtered through the window glass) and night darkness. The data without brackets in the Tables denote the total time required under these conditions for gel formation. Similar solutions were simultaneously stored in complete darkness (the times until gel formation are given in brackets in the Tables).

TABLE 3. TIME NEEDED FOR GEL FORMATION AFTER ADDITION OF A HALOGEN COMPOUND (X) TO A LATEX COPOLYMER STYRENE + *p*-DIMETHYLAMINOSTYRENE (3·25:1 mol) AT ROOM TEMPERATURE; THE LATEX CONTAINED 20 PER CENT OF DRY MATTER AND THE AMOUNT X WAS EQUIVALENT TO THE AMINO GROUP CONTENT IN THE POLYMER

Sample no.	X	Emulsifier	Gelation time
93	2,2,2-Trichloroethanol	Potassium laurate	10 min (10 hr)
94	2,2,2-Trichloroethanol	Sodium mersolate	10 min (10 hr)
95	1,2,3,4-Tetrachlorobutane	Potassium laurate	20 min
96	Trichlorobromomethane	Sodium mersolate	5 min

By acting with halogens and compounds of the elements of groups 3–8 of the periodic table containing one or more halogen atoms on polymers with a small number of tertiary amino groups in the polymer chain, it was possible to bind several identical or different macromolecules while preserving their solubility.

The viscosity of the benzene solution of poly(*p*-dimethylaminostyrene) alone did not increase in light until after 14 days; the viscosity of solutions of the other polymers remained unchanged even after 30 days.

An investigation of the reaction mechanism of tertiary amino groups of a polymer with halogen compounds is now in progress.

TABLE 4. TIME NEEDED FOR GEL FORMATION AFTER MIXING A SOLUTION OF 0·15 g POLYMER WITH A CHEMICALLY BOUND HALOGEN (X) IN 3 cm^3 BENZENE WITH A SOLUTION OF 0·15 g POLYMER WITH *tert*-AMINO GROUPS IN 3 cm^3 BENZENE AT ROOM TEMPERATURE (THE TIMES NEEDED FOR EXPERIMENTS IN THE DARK ARE GIVEN IN BRACKETS). DMAS = *p*-DIMETHYLAMINOSTYRENE, DMAEA = 2-DIMETHYLAMINOETHYL ACRYLATE, DMAEMA = 2-DIMETHYLAMINOETHYL METHACRYLATE, MMA = METHYL METHACRYLATE, VCZ = N-VINYLCARBAZOL

Sample no.	$(X)_0$	Gelation time				
		PolyDMAS	PolyDMAEA	PolyDMAEMA	Poly(DMAEA + MMA)	Various amines
97–99	Poly-(2,2,2-trichloroethyl acrylate)	1 min	1 min		2 hr	
100–102	Poly-(1,2,2,2-tetrachloroethyl methacrylate)		3 days		30 hr	5 hr*
103	Poly-(styrene-co-1,2,2,2-trichloroethyl acrylate)	2 days				
104–106	Poly-(styrene-co-1,2,2,2-tetrachloroethyl methacrylate)		5 days		3 days	30 hr†
107–108	Poly-(styrene-co-trichloroethylene)	12 hr (1 day)				
109–110	Poly-(styrene-co-vinylidene chloride)	12 hr (1 day)				
111–113	Poly-(styrene-co-2,3-dichloropropane)	12 hr (3 days)		(3 days)		
114–117	Brominated polychloroprene		4 hr (1 day)		3 hr (12 hr)	
118	Poly(vinyl chloride)‡					1 day*

* polyVCZ.
† N,N-dimethylaniline.
‡ In tetrahydrofuran solution.

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Résumé—Les polymères solubles et les copolymères ayant des groupements amine tertiaires réagissent à la température ambiante avec les halogènes et les composés halogénés en donnant des systèmes réticulés. La réticulation se produit en solution, en émulsion et dans des mélanges de polymères, à la lumière ultra-violette et visible et à l'obscurité.

Sommario—Polimeri e copolimeri solubili, con gruppi aminici a legami terziari, reagiscono a temperatura ambiente con gli alogeni e loro composti dando luogo a sistemi con legami trasversali. Tali legami trasversali si formano in soluzioni, emulsioni e miscele di polimeri, in presenza di luce, raggi ultravioletti e all'oscurità.

Zusammenfassung—Lösliche Polymere und Copolymere mit gebundenen tertiären Amingruppen reagieren bei Rautemperatur mit Halogenen und Halogenprodukten unter Bildung vernetzter Systeme. Die Vernetzung erfolgt in Lösung, in Emulsion und in Polymermischungen, in ultraviolettem und sichtbarem Licht und im Dunkeln.