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**REACTIONS OF MACROIONS WITH ESTER AND CARBOXYLIC GROUPS OF POLYMERS**

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In the reaction of dianions with poly(methyl methacrylate), only an insignificant amount of insoluble crosslinked product is obtained. If, however, the concentration of grafting dianions approaches that of ester groups, the amount of poly(methyl methacrylate) which may thus be crosslinked becomes quite significant. Dications, too, can bring about crosslinking of only an insignificant number of poly(methyl methacrylate) chains. Carboxylic groups in poly(acrylic acid) react with dianions and dications in an anhydrous medium similarly to ester groups. On the other hand, in the presence of a cocatalytic amount of water dications are more readily bound to carboxylic groups, forming a covalent bond. The relatively highest efficiency was observed in the bond formation between dication and the poly[styrene-*alt*-(maleic anhydride)], both in an anhydrous medium and in the presence of H<sub>2</sub>O.

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Ester and carboxylic groups react readily with a great variety of anions and cations. In macromolecular chemistry some reactions of this type may be a source of difficulties, while others are useful — *e.g.*, for syntheses of graft copolymers<sup>1</sup>. The anionic polymerization of methyl methacrylate does not proceed without termination and transfer<sup>2</sup>. According to some authors, addition of the carbanion to the carbonyl group gives rise to inactive compounds<sup>3</sup>, trimers<sup>4</sup>, and “internal” complexes<sup>5</sup>; less basic oxygen-containing anions are formed from reactive carbanions<sup>6</sup>. Mitsengendler with coworkers<sup>7,8</sup> and Remp<sup>9</sup> used living anionic polystyrene in the grafting of poly(methyl methacrylate) (PMMA). Mitsengendler and Andreeva considers grafting as very efficient, almost quantitative<sup>7,8</sup>; they observed that the anion preferentially attacks PMMA chains which had already been attacked by anions<sup>7,8</sup>. Matzner bound poly( $\epsilon$ -caprolactam) anions to the copolymer of styrene with a small quantity of methyl methacrylate. In the presence of more than 1 mole % ester groups in the copolymer a crosslinked product was formed<sup>10</sup>. By acting with the dianion of  $\alpha$ -methylstyrene tetramer (containing Na<sup>(+)</sup> counter ions) on a solution of the poly(vinyl chloride) and PMMA mixture, a certain amount of uncrosslinked poly-(vinyl chloride)-*graft*-poly(methyl methacrylate) was formed<sup>11</sup>. Until now, the mechanism of grafting of poly(methyl methacrylate) with polystyrene carbanions has not been completely elucidated. Some results seem to suggest that this reaction

does not lead unambiguously to the formation of a covalent bond between the grafting and grafted polymer. There are not many findings reported about reactions of cations with ester bonds, and of macrocations with carboxylic groups. They come from the experience gained in reesterification reactions in organic chemistry<sup>12</sup>. In the patent literature there is a reference regarding formation of graft copolymers from polymers containing ester groups and of macrocations prepared from polymer anions by the transformation of ionic ends<sup>13</sup>.

In this report we try to shed some light on the efficiency of grafting. The isolation of block and graft copolymers from mixtures with homopolymers has not yet been generally solved. The extraction is inherently time-consuming, and often inaccurate. Separation of insoluble (crosslinked) fractions from soluble polymers and copolymers is a simpler procedure. We have therefore decided to use diions in grafting polymers which contain ester and carboxylic groups. These reactions should lead to the formation of three-dimensional insoluble copolymers, and thus provide more exact information about grafting.

## EXPERIMENTAL

*Characteristics of the polymers:* Poly(methyl methacrylate), commercial product of CHVZ Synthesia Semtin (Czechoslovakia), was prepared by polymerization in bulk; relative number molecular mass ( $\langle M_n \rangle$ ) 405 000. Both poly(acrylic acid) and poly[styrene-*alt*-(maleic anhydride)] were prepared on a laboratory scale by the precipitation (solution) polymerization in benzene initiated with dibenzoylperoxide,  $\langle M_n \rangle$  856 000 (2 000). All polymers used in this study were purified by reprecipitation and dried *in vacuo*.

*Preparation of diions and their interactions with polymers:* The experiments were performed at pressure between  $10^{-2}$  and  $10^{-3}$  Pa in reactors attached to a glass high-vacuum line. The tetra( $\alpha$ -methylstyrene) dianion was prepared by reacting  $\alpha$ -methylstyrene with redistilled sodium in tetrahydrofuran. The solution of the dianion was stored in a sealed storage vessel at 256 K and used 14 days after the synthesis at the latest<sup>14</sup>. Using this initiator and a calculated amount of styrene the polystyrene dianion,  $\langle M_n \rangle$  5 000, was prepared; by applying the same initiator and a known quantity of cyclic siloxanes the poly(dimethylsiloxane) dianion,  $\langle M_n \rangle$  10 000 to 40 000, was obtained. The siloxonium dication was prepared by the hydrolysis of dichlorodimethylsilane in the presence of a mixture of H<sub>2</sub>O and HClO<sub>4</sub>, followed by removal of volatile fractions *in vacuo*<sup>15</sup>; dilution with dry benzene was used for easier dosage. Polymerizations of tetrahydrofuran at 263 K, initiated with the siloxonium dication, yielded the polymer dication, *i.e.*, living poly(oxytetramethylene).

*Interactions of diions with polymers:* Reactors containing the polymer were sealed to the high-vacuum line and thoroughly dried before dosage of the solvent by distillation. Initiators and the co-initiator were introduced by means of syringes provided with polyethylene capillaries in the stream of pure nitrogen. After the components had been introduced, the reactor was cooled down with liquid nitrogen, evacuated and sealed off at the constriction (Fig. 1a). If the polymer diion was used instead of one of the initiators, two reactors were combined (Fig. 1b). The diion was prepared in one of the reactors, the polymer solution in the other, and both components were mixed *via* break-seal after sealing off the system from the line and thermostating.

*Isolation of the products and their extraction:* After the polymer had reacted with the diion, the reactor contents were placed in the excess of methanol, and the separated precipitate was dried to constant mass at room temperature and normal pressure. The dry precipitate (about 1.5 g) was extracted by stirring (8 h) with ethyl acetate or toluene (60 ml solvent), in a thermostated cylindrical extractor at 333 K. After stopping the stirring the solid phase was left to sediment or was centrifuged, the pure liquid fraction was taken and the solvent was evaporated. The extraction was repeated as long as the mass of such dry residue after evaporation was greater than 0.002 g; the process of extraction of the interaction products between PMMA and the tetra( $\alpha$ -methylstyrene) dianion is given as an example (experiment 8 in Table I) in Fig. 2. The joined dry residues after solvent evaporation were freed from the homopolymer of the cross-linking agent by further extraction employing the described procedure: Poly(dimethylsiloxane) was extracted with hexane, poly(oxytetramethylene) with 2-propyl alcohol. The composition of the soluble copolymers thus isolated was then determined. When following the interaction between poly(acrylic acid) and diions the extractions were carried out with 2-propyl alcohol in a Soxhlet apparatus.

The insoluble residues (the crosslinked polymers) were analyzed.

*Characterization of the products:* For the IR analysis the crosslinked polymers (insoluble residues after extraction) were ground in an Ardenn ball mill to grains  $\leq 60 \mu\text{m}$  and measured in Nujol. The concentration of the mixture and the thickness of the KBr-cell were chosen according to the intensity of signals. The apparatus was UR-10, Zeiss, Jena.

GPC measurements were performed with a GPC/ALC (Waters) apparatus provided with three columns packed with Styragel, porosity  $10^4$ ,  $10^6$ , and  $10^7$  nm. The columns were calibrated using a set of polystyrene standards having a known molar mass; the samples were introduced in the form of 0.25% solutions in tetrahydrofuran. The apparatus was provided with two detectors: a UV detector operating at the wavelength 254 nm and a differential refractometer. The average

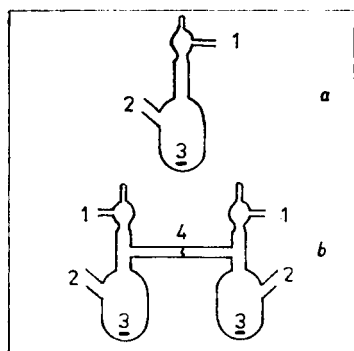


FIG. 1

Reactors for the interaction between diions and polymers: 1 connection with high-vacuum line, 2 opening, sealed after introduction of polymer, 3 stirrer, 4 break-seal

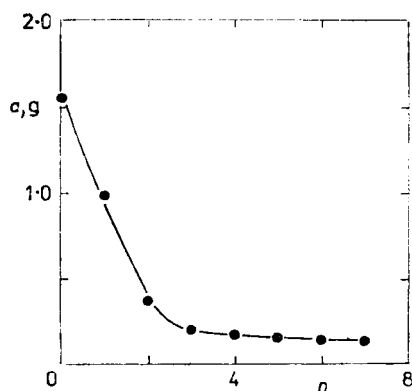


FIG. 2

Process of extraction of the interaction product of PMMA with the tetra( $\alpha$ -methylstyrene) dianion;  $a$  is mass of the insoluble fraction,  $n$  is the number of extractions of ethyl acetate (Exp. No. 8, Table I)

relative molar masses were calculated using universal calibration with constants according to Yan *et al.*<sup>16</sup>.

## RESULTS AND DISCUSSION

Coloured carbanions quickly lose their colour in contact with dissolved PMMA. The rate of discolouration is probably diffusion-controlled: If gel-like particles are formed on mixing, the rose-red colour of their interior lasts sometimes as long as several tens of minutes. The insoluble gel fraction eventually assumes the colour of

TABLE I

Reaction of 1.5 g PMMA (3.7  $\mu\text{mol}$ ; relative mol. mass 405 000) with polymer dianions in 50  $\text{cm}^3$  tetrahydrofuran at 297 K. Symbols:  $r_a$  molar ratio of ester group and anion in the reaction mixture,  $Y$  insoluble (crosslinked) fraction in methanol and ethyl acetate (mass % calculated with respect to starting PMMA),  $c_M$  molar content of methacrylate units in the insoluble fraction

Exp. No.	Dianion		[Dianion]	$r_a$	Reaction time, days	$Y$ mass %	$c_M$ mole %
	$\langle M_n \rangle$	$\mu\text{mol}$	[PMMA]				
Reaction with tetra( $\alpha$ -methylstyrene) dianion							
1	472	45	12	166.7	12	3.4	—
2	472	90	24	83.3	12	2.0	—
3	472	170	46	44.1	12	3.3	—
4	472	900	243	8.3	4	0.5	—
5	472	1 350	365	5.6	12	24.7	—
6	472	900	732	2.8 <sup>a</sup>	12	47.6	56
7	472	750	1 700	1.2 <sup>b</sup>	12	43.5	—
8	472	270 <sup>c</sup>	73	27.7	12	9.2	—
9	472	540 <sup>d</sup>	146	13.9	12	20.4	61
Reaction with polystyrene dianion							
10	5 000	350	95	21.4	2	0.6	—
11	5 000	400	108	18.8	12	9.2	73
Reaction with $(^-)\text{O}-\text{Si}(\text{CH}_3)_2-\sim-\text{Si}(\text{CH}_3)_2-\text{O}(-)$							
12	40 000	90	24	83.3	2	0.7	96 <sup>e</sup>
13	21 000	180	49	41.7	2	1.0	91 <sup>e</sup>
14	10 000	250	68	30.0	2	0.1	94 <sup>e</sup>

<sup>a,b</sup> Starting amount of PMMA <sup>a</sup> 0.5 g, <sup>b</sup> 0.18 g (in 10  $\text{cm}^3$  tetrahydrofuran). <sup>c,d</sup> Introduced in three portions: <sup>c</sup> 90  $\mu\text{mol}$ , <sup>d</sup> 180  $\mu\text{mol}$ . <sup>e</sup> In the fraction soluble in toluene after extraction with hexane.

conjugated systems. The effect of dianions — short (tetra( $\alpha$ -methylstyrene)) or longer (polystyrene,  $(^{-})\text{O}-\text{Si}(\text{CH}_3)_2-\sim-\text{Si}(\text{CH}_3)_2-\text{O}^{(-)}$ ) leads to only a small amount of crosslinked fractions formed (Table I). A gradual triple supply of dianion for PMMA, in which the first additions would consume water that might be present, also does not result in an important crosslinking of PMMA (experiment 8). Only using an enormously high concentration of ions, approaching those of ester groups, is it possible to achieve network formation from a major fraction of the starting quantity of PMMA (experiments 5; 6; 7, Fig. 3). The GPC record of the soluble product in experiment 10 (total ethyl acetate extract from the product insoluble in methanol, after removal of the homopolymer of the crosslinking agent), obtained by means of the RI and UV detectors (Fig. 4), proves that the polystyrene dianion attacks preferentially the low-molecular mass fractions of PMMA, and that the molecular mass of copolymer macromolecules is more than an order of magnitude higher than that of the starting polystyrene dianion.

We believe that the experimental findings may be explained by Scheme 1 (counter ions have been omitted in the scheme). Grafting proceeds by reaction (B); the same reaction occurs in the crosslinking, if each end of the dianion reacts with ester groups on various PMMA macromolecules in the same way. Gel formation displaces all the equilibria — (A), (B), and (C). Reaction (C) shifts the carbanion to the PMMA

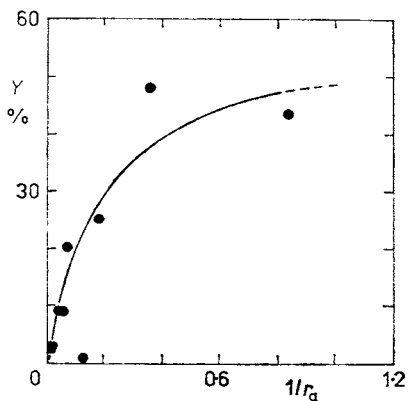


FIG. 3

Dependence of the insoluble fraction  $Y$  (mass % calculated with respect to the starting PMMA) on the molar ratio of anion and ester group,  $r_a$ , in the reaction of PMMA with tetra( $\alpha$ -methylstyrene) dianion

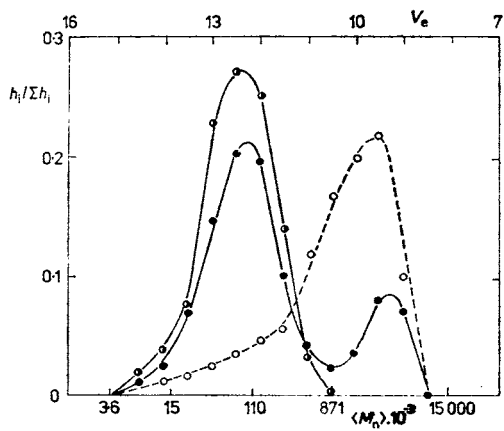
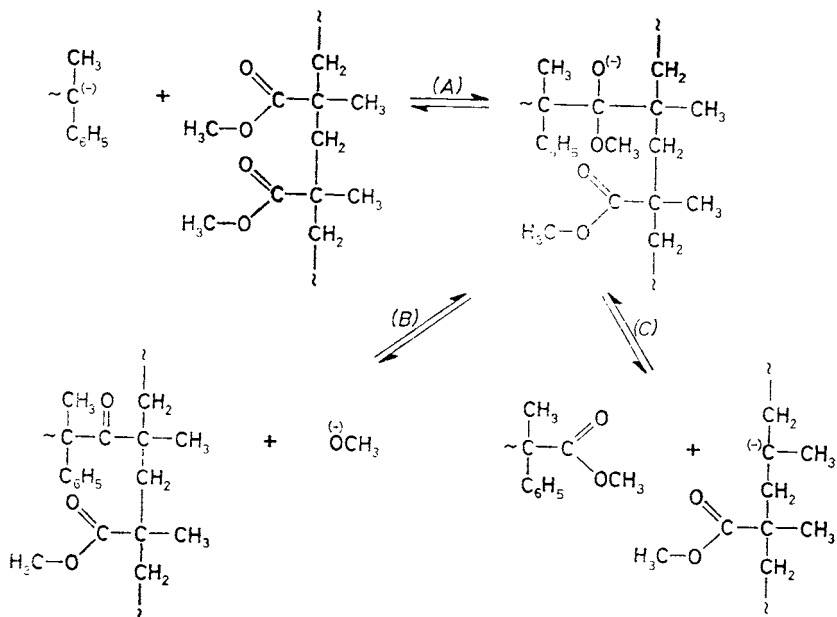


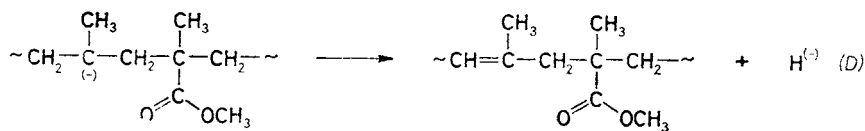
FIG. 4

GPC record of the soluble part of the interaction product between polystyrene dianion and PMMA (Exp. No. 10, Table I):  $\circ$  original PMMA;  $\bullet$  RI record (recorded both PMMA and polystyrene);  $\ominus$  UV record (recorded only polystyrene containing chains)



SCHEME 1

chain. The formation thus arising may react with the ester groups (analogy to reaction (A) or split off the hydride ion (reaction (D)).



If ester groups near the double bond react similarly, rather long, yellow-rose blocks of chains with conjugated double bonds may be formed. The low crosslinking efficiency may of course also be due to the participation of some other reactions, such as displacements of hydride ions (protons) from the anionic centre (polymer chain), or reactions (B) of both ends of the dianion with one PMMA macromolecule, or some processes as yet unknown.

Interaction between PMMA and dication also gives rise to only a small quantity of an insoluble product — crosslinked polymer (Table II). The poly(oxytetramethylene) dication grafts the PMMA chain (*cf.* analysis of the soluble fractions in experiments 8, 9, 10). It is quite likely, therefore, that also low-molar mass dication become fixed with covalent bonds to the polymer with which they interact.

Table III summarizes results obtained in the interaction of poly(acrylic acid) or poly[styrene-*alt*-(maleic anhydride)] with diions. The dication in an anhydrous medium brings about the crosslinking of only an insignificant quantity of poly(acrylic acid) (experiments 5–8), comparable with that of PMMA crosslinked with the anions (*cf.* Table I). The dication in the presence of a cocatalytic amount of

TABLE II

Reaction of 1.5 g (3.7  $\mu\text{mol}$ ) PMMA (relative mol. mass 405 000) with polymer dications in 50  $\text{cm}^3$  tetrahydrofuran. Symbols:  $r_c$  molar ratio of ester groups and cation in the reaction mixture,  $Y$  insoluble (crosslinked) fraction in methanol and ethyl acetate (mass % calculated with respect to the starting PMMA),  $c_M$  molar content of methacrylate units in the graft polymer, *i.e.* in the soluble fraction in ethyl acetate freed from poly(oxytetramethylene) by extraction with 2-propyl alcohol

Exp. No.	Dication		[Dication]	$r_c$	$T$ K	Reaction time, days	$Y$ mass %	$c_M$ mole %
	$\langle M_n \rangle$	$\mu\text{mol}$	[PMMA]					
Reaction with $(^+)\text{Si}(\text{---O---Si})_5\text{---O---Si}^{(+)}$								
1 <sup>a</sup>	502	92	24	84	297	2 <sup>c</sup>	0.1	—
2 <sup>a</sup>	502	250	68	30	297	2 <sup>c</sup>	0.1	—
3 <sup>a</sup>	502	250 <sup>b</sup>	68	30	297	2	1.0	—
4 <sup>a</sup>	502	250 <sup>b</sup>	68	30	297	12	2.3	—
Reaction with poly(oxytetramethylene) dication								
5	22 500	45	12	167	297	5	1.1	—
6	10 000	50	14	150	263	3 <sup>c</sup>	0.1	—
7	17 500	90	24	84	263	6	7.0	—
8	17 500	90	24	84	297	3 <sup>c</sup>	3.2	98
9	17 500	90	24	84	297	3	1.5	94
10	17 500	90	24	84	297	6	1.5	95
11	22 000	90	24	84	297	5	0.6	—
12	22 000	250	68	30	297	5	1.6	—
13	22 000	250 <sup>b</sup>	68	30	297	5	1.3	—
14	45 000	250	68	30	263	6	0.1	—
Reaction with $(^+)\text{Si}(\text{---O---Si})_5\text{---O---Si}^{(+)}$								
15	502	90	24	84	297	5	2.1	—
16	502	250 <sup>b</sup>	68	30	297	5	0.9	—

<sup>a</sup> In 50  $\text{cm}^3$  benzene. <sup>b</sup> Used with 130  $\mu\text{mol}$   $\text{H}_2\text{O}$ . <sup>c</sup> Hours.

H<sub>2</sub>O and the dianion react with poly(acrylic acid) in benzene solution, giving rise to a considerable amount of an insoluble product. Poly[styrene-*alt*-(maleic an-

TABLE III

Reaction of 1.0 g (1.2 μmol) poly(acrylic acid) (relative mol. mass 856 000) or 1.0 g (1.2 μmol) poly[styrene-*alt*-(maleic anhydride)] (relative mol. mass 2 000) with polymer diions at 297 K. Symbols:  $r_1$  ratio of the molar concentration of the carboxylic or anhydride group to the molar concentration of the ion,  $Y$  insoluble (crosslinked) fraction in methanol and 2-propyl alcohol (mass % calculated with respect to the starting polymer),  $c_p$  molar content of the starting polymer (P) in the insoluble fraction

Exp. No.	Diion μmol	H <sub>2</sub> O	[Diion] [P]	$r_1$	Reaction time, days	$Y$ mass %	$c_p$ mole %
Reaction of poly(acrylic acid) with tetra(α-methylstyrene) dianion ( $\langle M_n \rangle$ 472) in 20 cm <sup>3</sup> benzene							
1	45	—	39.0	154	5	3.8	—
2	90	—	77.0	77	2	14.5	—
3	90	—	77.0	77	5	10.0	18
4	180	—	154.0	39	5	22.5	—
Reaction of poly(acrylic acid) with $\begin{matrix}   \\ (+)Si(-O-Si)_5-O-Si(+) \\   \end{matrix}$ ( $\langle M_n \rangle$ 502) in 20 cm <sup>3</sup> benzene							
5	90	—	77.0	77	2	1.1	—
6	90	—	77.0	77	5	0.6	—
7	250	—	214.0	28	2	1.4	—
8	250	—	214.0	28	5	2.3	—
9	90	45	77.0	77	5	14.6 <sup>a</sup>	—
10	90	45	77.0	77	12	37.5	—
11	250	130	214.0	28	5	32.1 <sup>a</sup>	—
Reaction of poly[styrene- <i>alt</i> -(maleic anhydride)] with $\begin{matrix}   \\ (+)Si(-O-Si)_5-O-Si(+) \\   \end{matrix}$ ( $\langle M_n \rangle$ 502) in 20 cm <sup>3</sup> tetrahydrofuran							
12	90	—	0.2	27	5	46.9 <sup>b</sup>	63
13	90	45	0.2	27	5	43.4 <sup>b</sup>	66
14	250	130	0.5	10	3	22.6 <sup>b</sup>	68
15	250	130	0.5	10	5	59.5 <sup>b</sup>	66

<sup>a</sup> Reaction mixture not precipitated with methanol, solvent evaporated (*cf.* Experimental).

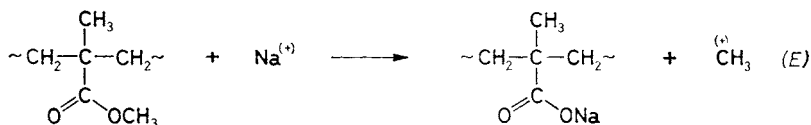
<sup>b</sup> Fractions after extraction with ethyl acetate.



hydride)] also gives a large amount of an insoluble product (experiments 13–15), also by a reaction in the anhydrous medium and with H<sub>2</sub>O. The dication may react in this case both with anhydride groups and with benzene rings<sup>17</sup>.

Diions never cause the crosslinking of the whole polymer (copolymer) with which they react. Hence, grafting probable also cannot proceed quantitatively. Thus, either both ends of the diions react with the ester (carboxylic) groups of a single polymer macromolecule while giving rise to covalent bonds (and thus to copolymer of a very interesting structure), or a large part of the ions is deactivated in another way. It is evident that in reactions of oligomer or polymer ions trivial effects may be operative, such as steric hindrances (especially in the case of poly[styrene-*alt*-(maleic anhydride)]), in which the styrene unit impedes the bonding of adjacent carboxylic groups with a short dication), electronegativity of the C and O atoms in various groups, and chain association (shape of coils, especially in the case of poly(acrylic acid)). Analyses of insoluble products in experiments 6, 9, 11 in Table I show that less than one half of the crosslinking anion is bound in them. The rest grafts PMMA (the grafted fraction remains soluble), and/or both ends of the dianion become deactivated, perhaps by reaction (C) in Scheme 1, or by a transfer of the hydride ion or proton. So far, there is no direct evidence which would allow us to explain the chemism of these observations.

In IR spectra of the interaction products between PMMA and dications some distinct bands of carboxylates can be seen. Salts of carboxylic acids may be formed by a reaction of counter ions (Na<sup>(+)</sup>) with ester groups (reaction (E)).



(+) CH<sub>3</sub> would be immediately neutralized with carbanions and/or H<sup>(-)</sup>, OR.

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