

# Reactions of macroions leading to block and/or graft copolymers. Macroion transformation: anion $\rightarrow$ cation and cation $\rightarrow$ anion

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(Received 16 May 1984; revised 11 November 1984)

The efficiency as well as the feasibility of a transformation of ionic polymerization centres to those possessing an opposite charge, has been examined. The transformation was effected via the interaction of the polymeric dianion (dication) being transformed, with a molar excess of an oligomeric dication (dianion). The result of the interaction was evaluated by measuring the molecular weight of the product. The transformation of anionic ends to cationic ends (or the reverse) proceeds smoothly at a twofold excess of the transforming diion. When this excess is lower then combination of oppositely charged ends of both reactants takes place simultaneously with transformation. The transformation of dianionic living polystyrene ( $M_n = 5000$ ) (dicationic poly(tetramethylene oxide),  $M_n = 6000$ ) to dicationic (dianionic) product deviates only slightly from the theoretically assumed course; the transformation of diions of higher molecular weight ( $M_n = 17-30 \times 10^3$ ) to polymers with oppositely charged ends obeys reasonably the assumed kinetics only at a two-fold excess of the transforming oligomer; below this ratio differences are more pronounced. The polymerization of suitable monomers on the transformed centres gives rise to block copolymers. Detailed structures of these copolymers have not yet been elucidated due mainly to difficulties in separation of block and homopolymers from mixtures.

(Keywords: transformation; ionic centres; anion; cation; poly(tetramethylene oxide); polystyrene)

## INTRODUCTION

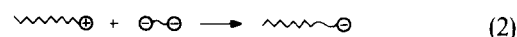
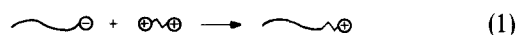
The preparation of block (graft) copolymers, the blocks (grafts) of which are mutually chemically different (especially if they differ in hydrophobic-hydrophilic character) is, in most cases, feasible only via the condensation of suitable macromers (telechelic polymers) or through a direct combination or other reaction of macroions. Another possibility, published in our previous papers<sup>1-8</sup>, consists of the reaction of polymeric ions whose charge was changed according to requirements.

The macroion transformation to one of opposite charge has been the subject of several authors' study. The anion-cation transformation process (or the reverse) requires a double electron transfer which cannot be achieved directly. For this reason, attention has been directed to achieving those ends via a series of reactions. Yamashita<sup>9</sup> reported on the transformation of polystyrene macroions to corresponding cations by employing a multiple-step process involving oxirane, adipoylchloride, 1-bromo-2-hydroxyethane and  $\text{AgClO}_4$ . Franta *et al.*<sup>10</sup> made use of the following reaction sequence for the transformation of anions to cations. The carbanions of living polystyrene were transformed to acylchloride ends by treatment with phosgene. Terminal carbocations were then obtained by reaction with  $\text{AgSbF}_6$ . British authors<sup>11-14</sup> have studied the anion  $\rightarrow$  cation transformation in some detail. The principle of their approach was based on the conversion of the carbanions to terminal bromide ions. This was effected either by direct treatment with elemental bromine<sup>11</sup> or by reaction with a suitable dihalogenide such as *m*- or *p*-di(bromomethyl)benzene after converting

the anionic centre to a polymeric Grignard compound. In the second step of the transformation process the bromide thus formed was reacted with the silver salt of a superacid to give polymeric carbocations.

Until recently, the cationic to anionic transformation has not been effected in satisfactory yields. Though Abadie *et al.*<sup>14,15</sup> suggested a system of reactions allowing the transformation of polymerizing tetrahydrofuran oxonium centres to carbanions (using the lithium salt of  $\beta$ -methoxystyrene and subsequently of butyllithium), the efficiency of this process is low.

We have shown previously<sup>1,6-8</sup> that macroion charge transformation may successfully be effected in high yield when the macroion is combined with an oppositely charged oligomeric diion. If one denotes the anionically (cationically) growing chain as  $\sim$  ( $\sim$ ) and the oligomeric dianion (dication) as  $\ominus\ominus$  ( $\oplus\oplus$ )  $\downarrow$ , the counterions not being presented, then the transformation may be described as follows:

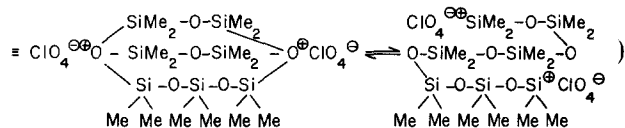


The results of our experiments concerning these reactions are the subject of this paper.

## EXPERIMENTAL

The source of the basic materials, namely styrene,  $\alpha$ -methylstyrene ( $\alpha$ -MeS), tetrahydrofuran (THF), methanol and  $\text{N}_2$ , as well as their modes of purification and

manipulation have been described in previous communications<sup>1-7</sup>. The preparation of oligomeric dianion (dication), sodium salt of  $\alpha$ -MeS tetramer  $\equiv$  DIA (siloxonium dication  $\equiv$  DIC  $\equiv$



has already been reported in some detail<sup>16,17</sup>.

The molecular weights were measured in THF using a Knauer membrane osmometer and by gel chromatography on a Waters Assoc. GPC 244 equipment running at ambient temperature. The instrument was fitted with Styragel packed columns (porosity  $10^2$  and  $10^4$  nm, respectively).

The preparation of oligomeric diions, macroions and their transformation were carried out in all-glass apparatus attached to a high-vacuum ( $10^{-2}$ – $10^{-3}$  Pa) line.

*Procedure for cation→anion→cation transformation*

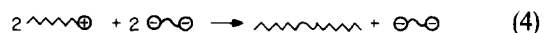
The reactor (see Figure 1) was sealed to the line at **a** and, after drying, was filled with dry  $N_2$ . The sampling port was created by cutting off the end of the thin tube at **b**. Through this opening 0.18 mmole of DIC (in 0.3 cm<sup>3</sup> of benzene) was introduced into A under a constant counter-flow of  $N_2$ . After sealing the tube and cooling down A with liquid nitrogen the reactor was pumped down, benzene distilled off and THF (20 cm<sup>3</sup>) added by distillation. The whole apparatus was sealed off and removed from the line at **c**. The apparatus was then resealed to the vacuum line at **a'**. Upon drying, filling with  $N_2$  and making the sampling port at **b'**, 0.18–0.36 mmole of DIA in THF (2 cm<sup>3</sup>) was introduced into B. After sealing the sampling port at **b'** and sealing off the line at **c'**, the whole apparatus was maintained at 263 K for 24 or 72 h. After this period the living poly(tetramethylene oxide) solution was introduced into the solution of transforming dianions through the break-seal. This experimental arrangement minimizes the formation of long chains by combination of ends carrying opposite charges; this process always takes place if some of the ions are not present in excess. A sleeve around the neck of bulb B reduces the internal area covered by viscous polymer solutions.

Transformation of anion→cation was simpler in apparatus design since the anionic polymerization of styrene is very rapid. The reactor (see Figure 2) attached to the vacuum line at **a** was dried and 20 cm<sup>3</sup> of THF was distilled into the bulb B. The apparatus was then cooled to 205 K, filled with dry  $N_2$ , the end of tube was cut off at **b** and through this port a benzene solution of DIC was injected into A and DIA was introduced into THF in B. Immediately afterwards, a calculated amount of styrene was added to B while stirring vigorously. The sampling of styrene by a syringe leads to a more homogeneous macroanion product than the distillation of styrene from a storage vessel into bulb B. All these operations were carried out under constant nitrogen counter-flow. After the polymerization of styrene, which took only a few seconds, the reactor was immersed in liquid nitrogen, sealed off the line at **c**, warmed to 263 K and the solution of living polystyrene was transferred to the dication in the bulb A.

The products of the macroion interactions were precipitated and washed with methanol. After drying to constant weight, analyses were carried out. Further details concerning the experimental procedure are included, whenever necessary, in the text to follow.

RESULTS AND DISCUSSION

Contact of macroion with excess of the transforming diion may lead either to a simple transformation according to equations (1) and (2), respectively, or to the formation of a non-ionic three-component block and a residual oligomeric diion:



The system containing triblocks, dianion and solvent is difficult to analyse and to obtain information about the relative importance of reactions (1) and (3) or (2) and (4).

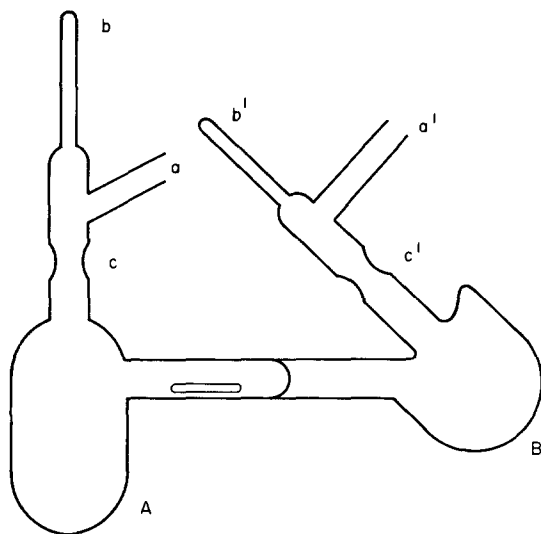


Figure 1 Scheme of apparatus for cation→anion transformation: a, points of attachment to the line; b, sampling point; c, seal off point

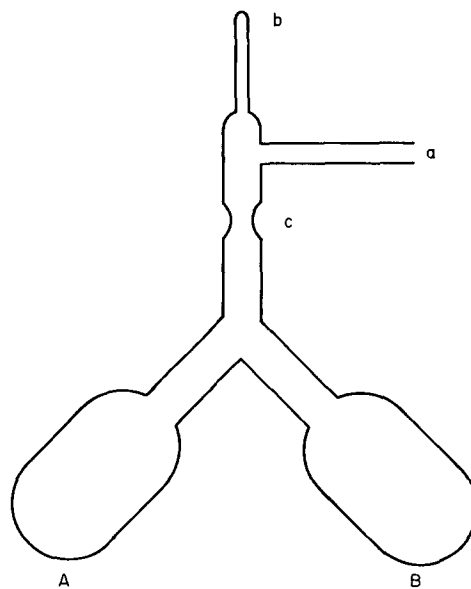
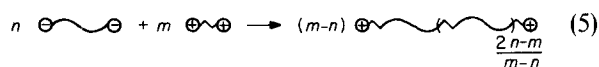
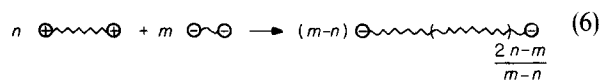


Figure 2 Scheme of apparatus for anion→cation transformation. For a, b, and c, see Figure 1

For this reason we preferred to study the transformation of such diions which give, in the absence of side reactions and under the condition  $n < m \leq 2n$ , the following molecules:

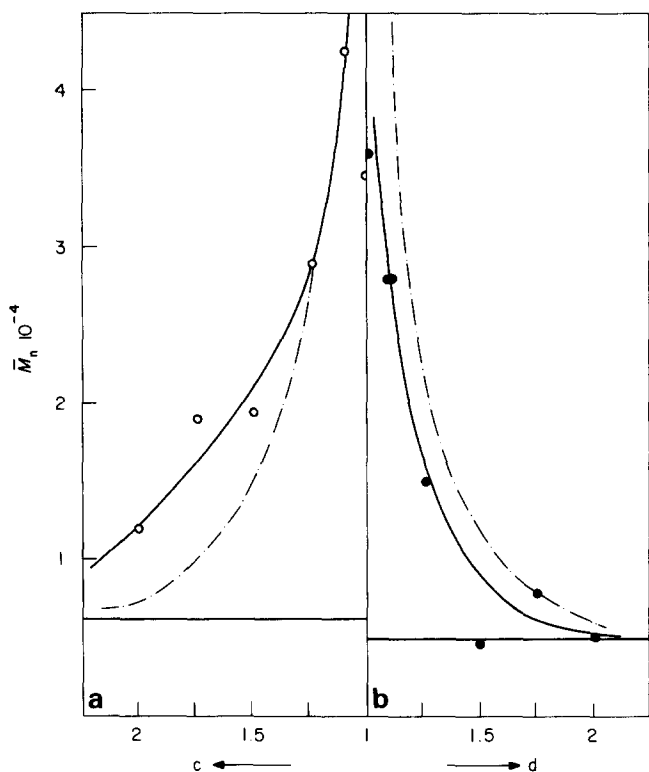


or



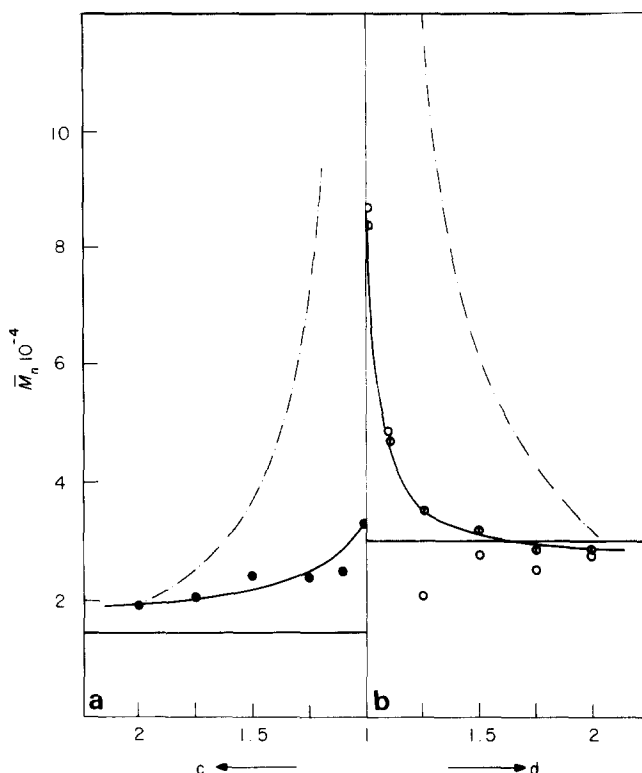
These are much longer than triblocks (if  $n \approx m$ ). When  $m = 2n$  transformed macroions result, the molecular weights of which are increased by the attachment of the two transforming oligomer diions only. The differences in macromolecule lengths of the products should therefore be greater, thus enabling a more precise evaluation. It seems very likely that the results of diion transformations may be applied to monoion transformations. The repulsive powers existing between the two identically charged ends of polymeric diion should not exhibit a significant effect upon the transformation.

The dependence of the degree of polymerization of the transformation products formed from  $\oplus$ polytetramethylene oxide $\ominus \rightarrow \alpha\text{MeS}(\alpha\text{-MeS})_3\text{-PTHF}-(\alpha\text{-MeS})_3\text{-MeS}^\ominus$  as well as  $\ominus$ polystyrene $\ominus \rightarrow \text{Si-O}-(\text{Si-O})_6\text{-PS-}$



**Figure 3** Transformation of  $\text{ClO}_4^\ominus \text{PTHF}_{90} \text{ClO}_4^\ominus$  to  $\text{Na}^\oplus \alpha\text{-MeS}_4\text{-PTHF}_{90}(\alpha\text{-MeS}_4\text{-PTHF}_{90})\alpha\text{-MeS}_4\text{Na}^\oplus$  (a) and  $\text{Na}^\oplus \text{PS}_{50} \text{Na}^\oplus$  to  $\text{ClO}_4^\ominus \text{Si-D}_6\text{-PS}_{300}(\text{D}_6\text{Si-PS}_{300})\text{D}_6\text{Si}^\oplus \text{ClO}_4^\ominus$  (b)

Diagram (a) represents the molecular weight dependence of polymeric dication ( $9 \text{ mmole dm}^{-3}$ ) interaction product with oligomeric dianion, the molar ratio ranging from unity to two-fold excess of dianion. Curve (b) demonstrates a similar dependence for the interaction of polymeric dianion ( $9 \text{ mmole dm}^{-3}$ ) with oligomeric dication. Molecular weights of initial polymeric diions are presented by thin horizontal lines. Arrow c, molar excess of DIA; arrow d, molar excess of DIC



**Figure 4** Transformation of  $\text{ClO}_4^\ominus \text{PTHF}_{243} \text{ClO}_4^\ominus$  to  $\text{Na}^\oplus \alpha\text{-MeS}_4\text{-PTHF}_{243}(\alpha\text{-MeS}_4\text{-PTHF}_{243})\alpha\text{-MeS}_4\text{Na}^\oplus$  (a)

and  $\text{Na}^\oplus \text{PS}_{300} \text{Na}^\oplus$  to  $\text{ClO}_4^\ominus \text{Si-D}_6\text{-PS}_{300}(\text{D}_6\text{Si-PS}_{300})\text{D}_6\text{Si}^\oplus \text{ClO}_4^\ominus$  (b)

Legend to Figure 3 is valid also in this case. Molecular weight: ( $\ominus$ ) osmometrically; ( $\circ$ ), ( $\bullet$ ) by g.p.c.

$(\text{Si-O})_6\text{-O-Si}^\oplus$  are presented in Figures 3 and 4. As expected, the longest chains are formed at a ratio of transformed to transforming ions of unity. At a two-fold excess of the transforming agent the resulting molecular weight is only slightly higher with regard to  $M_n$  than the original diion being transformed.

The combination of diions is, in fact, a kind of polycondensation influenced by electrostatic forces resulting from oppositely charged end groups of the reacting molecules. Assuming the absence of side reactions, the number of blocks ('degree of polymerization') in the product can be expressed as follows<sup>18</sup>:

$$\sigma = \frac{[A] + [C]}{|[A] - [C]|} \quad (7)$$

A and C denoting dianion and dication, respectively. The molecular weight of the product, calculated from the number of blocks theoretically formed according to relation (7) is presented in Figures 3 and 4 as a broken line.

The agreement between theoretical and observed values is satisfactory in the case of relatively low-molecular weight macroions to be transformed (around  $M_n \sim 5000$ ) (see Figure 3). With the increasing length of macroions the efficiency of combination decreases<sup>7</sup> (see Figure 4, particularly Figure 4a). The discrepancies between theory and experiment are considerable at a molar ratio of transformed and transforming ions around unity. The position and slope of the whole experimental curve in Figure 4a, particularly in the higher molecular

**Table 1** Number of blocks, actual functionality and combination efficiency at equimolar diion concentration  $\eta$  (see Figures 1 and 2)

Parameter	Case 1a	1b	2a	2b
$\sigma$	13.1	12.1	3.8	7.2
$f_E$	1.85	1.83	1.47	1.72
$\eta$ (%)	92.4	91.8	73.7	86.1

**Table 2** Styrene polymerization proceeding on transformed centres<sup>a</sup>

Composition of copolymer (theoretical) <sup>b</sup>	$\bar{M}_n$ of product	
	Calculated	Experimental <sup>c</sup>
S <sub>178</sub> -THF <sub>243</sub> -S <sub>178</sub>	54 700	37 000
S <sub>193</sub> -THF <sub>243</sub> -S <sub>193</sub>	57 700	34 000
S <sub>193</sub> -THF <sub>243</sub> -S <sub>193</sub>	57 700	74 000

<sup>a</sup> Initial  $\oplus$ PTHF $\oplus$  having  $\bar{M}_n = 17\,500$  at concentration  $9\text{ mmole dm}^{-3}$  was transformed by  $18\text{ mmole dm}^{-3}$   $\ominus(\alpha\text{-MeS})_4^\ominus$  at 263 K

<sup>b</sup> Transforming oligomer neglected

<sup>c</sup> By g.p.c., evaluated according to ref. 13

region is, of course, influenced by the presence of a considerable amount of relatively low-molecular weight macrocycles formed during THF polymerization<sup>19</sup>. It has so far proved impossible to separate these macrocycles both from poly(tetramethylene oxide) containing living ends and from the combination products; the macrocycles significantly lower the measured values of the molecular weight. Thus the difference between the observed and theoretical course of the curve in Figure 4a should be smaller in the vicinity of a ratio equal the unity. A possible slow transfer during the three day THF polymerization, leading to the formation of monocations, cannot be excluded either.

Figure 4b demonstrates very well the feasibility of transformation even in the case of high molecular ions.

A formal similarity of combination, involving diions of opposite charges, to the polycondensation reaction enables the combination efficiency at equimolar concentration of both kinds of ions to be quantified. The following relationship holds<sup>20</sup>:

$$\bar{P}_n = \sigma = \frac{1}{1 - \frac{pf}{2}} = \frac{1}{1 - \frac{f_E}{2}} \quad (8)$$

(where  $p$  = relative number of functional groups that underwent the reaction; in our case  $p = 1$  and  $f$  represents the functionality of 'monomer'). The number of blocks,  $\bar{P}_n$ , was determined experimentally; it is thus sufficient to compare the theoretical functionality of each diion ( $= 2$ )

with that obtained experimentally ( $f_E$ ). This comparison is made in Table 1.

When a two-fold molar excess of the transforming agent is present then the theoretical and experimental values are very close (ratio  $(2n - m)/(m - n)$ , equations (5) and (6), approaches zero). This is indicative of a total transformation; the molecular weight of the product should otherwise decrease below that of the initial transforming ions as a consequence of the oligomer excess.

The polymerization of THF (styrene) proceeding on dications (dianions) formed by the transformation, leads to the formation of surface-active<sup>6</sup> triblocks, if one neglects the presence of the short sequences of the transforming oligomers. Attempts to separate homopolymers which may be present have failed due to the formation of micelles that preclude a more exact analysis<sup>2</sup>. The results of molecular weight determinations of the products are presented in Table 2. The accordance between the expected and observed values is not very satisfactory, this being attributed to the difficulties in analysis rather than to a poor efficiency of transformation.

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