Combinatination of polymer ions. Formation of block copolymer by reaction of low molecular dianions with oligomeric dications

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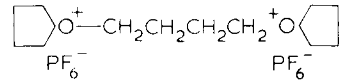
The combination of a polystyryl dianion with a silenium dicationic initiator leads to the formation of polymer whose backbone consists of alternating blocks of short siloxane chains and polystyrene. Similarly, the combination of polytetrahydrofuran dication with an α-methylstyrene dianion (α-methylstyrene tetramer) gives a block copolymer. Knowing the value of the molecular weight of a diionic component and that of the product it is possible to estimate the number of blocks in the polymer chain, i.e. 'the degree of polymerization' if each component is considered to be a 'monomer'. The application of relationships holding for polycondensation enables the overall average functionality of reacting diions to be calculated. When relatively low molecular components (*M.W. ca* 10^3) enter the reaction, the efficiency of combination exceeds the value of 95%. This value somewhat decreases with increasing molecular weight of reactants but it is always greater than 90%. When one of the combining diions is present in excess, shorter chains are formed in accordance with theoretical assumptions. The polydispersity of product is always higher than that of original components; neither temperature nor molecular weight of components exhibit a significant influence upon polydispersity.

INTRODUCTION

The combination of carbanion with carbocation or carboxonium ion may lead to the formation of a covalent bond. This principle was first employed by Berger *et al.*[1] as well as by Asami and Chikazawa[2] who combined living polystyrene (PS) dianion with living cationic polytetrahydrofuran (PTHF) to obtain block copolymer. The presence of a dication is necessary when multiblock chains are to be prepared. Yamashita *et al.* have reported on the preparation and use of *bis*-dioxoleniumperchlorate[3]. The product which is formed by the polymerization of tetrahydrofuran (THF) in the presence of this initiator contains two ester groups which might be preferably attacked by the carbanion end of the polystyrene chain. Yamashita *et al.*[4] therefore transformed the carbanions to less basic carboxylate ions by treating the former with CO_2. Although the procedure is rather complicated these authors first obtained multiblock copolymers by the process of combination.

Besides the already mentioned bis-dioxolenium perchlorate also some other different dications have recently been described; those formed from fluorosulphonic acids and THF[5].



prepared from THF and PF_5 [6], compounds formed from aralkylhalides and $AgClO_4$ or $AgPF_6$[7]. The first defined dication has been described by us[8,9]. It has a silenium character; a more detailed description of its preparation and properties has recently been published[10]. Using this dication it was possible to obtain block copolymers by combination[11,12] as well as to transform anionic living centres to cationic ones[13]. Similar work has been carried out simultaneously also in other laboratories. Burgess *et al.* have already published some interesting communications[14–18].

Block copolymers are strong interfacially active agents. Thus difficulties arise when attempts are made to separate homopolymers by extraction. To avoid these problems we have studied the combination of relatively low molecular diions with very short initiator diions. Under these conditions, only short blocks derived from the initiator are present in the basic macromolecule. In the first approximation the product may therefore be considered as homopolymer. We have used polystyrene and polytetrahydrofuran as representatives of anionic and cationic blocks, respectively.

EXPERIMENTAL

Chemicals

Styrene and α-methylstyrene were purified from the stabilisers, dried over CaH_2 and distilled in a high-vacuum apparatus. The middle fraction containing more than 99.9% of monomer was collected.

Tetrahydrofuran, pure, product of VEB Laborchemie Apolda, GDR. Prior to use it was distilled three-times on a high-vacuum line from a green solution of naphthalene sodium. The 339.5K middle fraction was collected, the content of impurities being lower than 0.1%.

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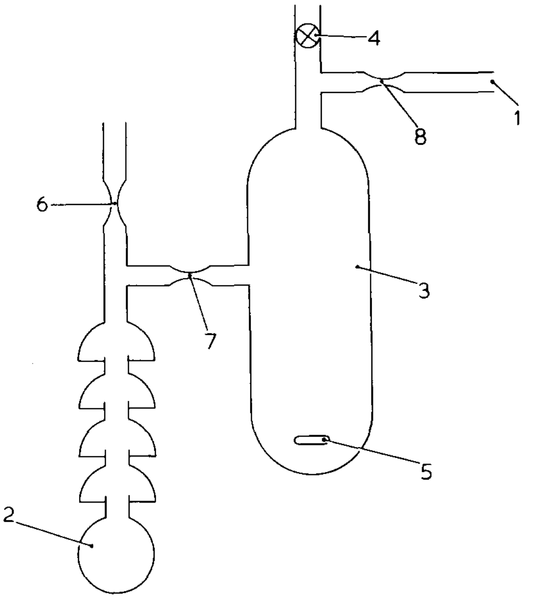


Figure 1 Apparatus for dianion preparation. 1, vacuum line attachment; 2, sodium vessel; 3, reaction vessel; 4, three-way stopcock; 5, stirrer; 6–8, seal-off points

Nitrogen was produced by Technoplyn Ostrava; the commercial gas containing *ca* 60 ppm of oxygen was passed through columns packed with R3-11 BASF catalyst and molecular sieve Nalsit 4A. After purification the water and oxygen contents were reduced to *ca* 1 ppm.

The synthesis of sodium salt of α-methylstyrene tetramer dianion was carried out in the apparatus shown in *Figure 1.* Sodium was distilled first from the storage bulb into the reaction vessel. The bulb was then sealed off and THF as well as α-methylstyrene were collected employing bulb-to-bulb distillation into the reaction vessel in such amounts as to enable the formation of the sodium salt of α-methylstyrene tetramer at concentration *ca* 0.25 mol/dm^3. The reaction vessel was then filled with nitrogen and sealed off. The initiator was not stored longer than 100 hours at 263K. The concentration of carbanions was determined acidimetrically and/or spectrophotometrically prior to each run.

Silenium dication: the preparation of $ClO_4{}^{\ominus}\ {}^{\oplus}Si(CH_3)_2–(O–Si(CH_3)_2–)_5O–Si^{\oplus}(CH_3)ClO_4{}^{\ominus}$ was described in our previous works[8–10]. The dication was examined by means of n.m.r. The comparison of hydroxyl and aromatic hydrogens (internal standard) permits estimation of the concentration of Si–OH groups which was within 0–2% mol with regard to $\sim Si^{\oplus}ClO_4{}^{\ominus}$ content.

Apparatus and procedure

All experiments were carried out on a high-vacuum line at 10^{-3}–10^{-4} Pa. The apparatus could also be filled with pure nitrogen which allows the introduction of components as well as taking samples without contaminating the system. Dry and purified monomers were distilled first into a calibrated tube which was the part of the line. Reaction vessels were dried under continuous pumping for 8–10 hours and sealed off after the end of experiment.

Polymerization of THF. The reaction was carried out using the apparatus which principally corresponded to the left hand part of the reactor shown in *Figure 2.* The solution of silenium dication in benzene was sampled by means of a hypodermic syringe while the system was continuously being flushed with nitrogen. The solvent was then removed *in vacuo* and the monomer was distilled. The reaction vessel was sealed off and THF was left to polymerize at a selected temperature for a given period of time. The reaction was stopped by precipitating the polymer with 2% methanolic solution of ammonia. The conversion of THF to polymer was, within the period of our experiments, directly proportional to time; the rate of initiation is high[12]. These runs were used as reference to determine the molecular weight of the dications. The values obtained were compared with a *M.W.* – conversion diagram[12] and a very satisfactory agreement was found.

Styrene polymerization. A known amount of THF and styrene was distilled into the reactor described above. The solution was thermostatted at 243 K and the sodium salt of α-methylstyrene tetramer dianion was added by a hypodermic syringe under the stream of nitrogen. Although the polymerization was finished within several seconds the polymer was isolated after 1 h. The molecular weight of polystyrene determined by g.p.c. was practically identical with the theroretical value, the coefficient of polydispersity being within 1.1–1.5 (depending on molecular weight and consequently on the time of initiator sampling).

The combination of block polymers was performed in the reactor shown in *Figure 2.* The calculated amount of cationic initiator in benzene was transferred by a hypodermic syringe into a left hand part of apparatus under continuous flushing with nitrogen.

After removing the solvent *in vacuo,* THF was distilled into the reactor, degassed and the vessel was sealed off. The monomer was left to polymerize at selected temperature. The same procedure was employed for filling the right hand part of apparatus with $^{\oplus}Na^{\ominus}(\alpha\text{-MeS})_4{}^{\ominus}\,Na^{\oplus}$. The tetramer was diluted with THF, the monomer introduced and the apparatus sealed off. As soon as the desired conversion was achieved (viscosity increase) the break seal separating both bulbs was broken and the components were mixed together. After 24 h the sample was isolated, washed several times with methanol, dried to constant weight and analysed.

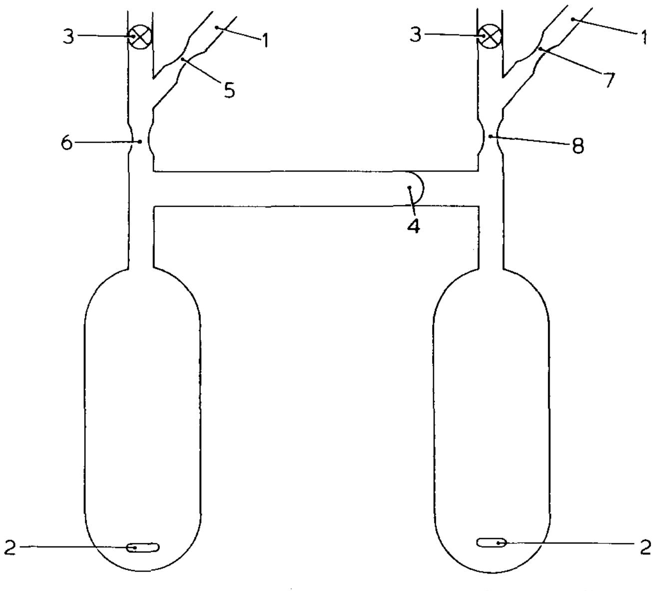


Figure 2 Reactor for combination of macroions. 1, vacuum line attachments; 2, stirrers; 3, stopcocks; 4, bubble break seal; 5–8, seal-off points

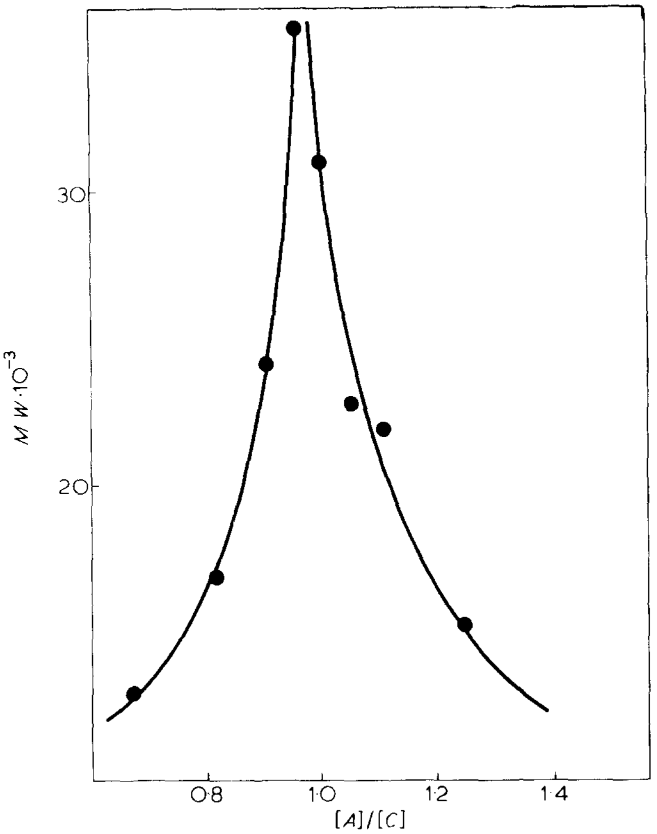


Figure 3 Dependence of molecular weight on ratio of dianion to dication. Temperature of styrene polymerization and combination 233 K. A = polystyryl dianion, $\bar{M}_A$ = 5200–5600; C = silenium initiator

Evaluation of products

G.p.c. analyses were carried out at ambient temperature using a Waters Associates instrument. The columns were packed with Styragel 10^3 and 10^5 nm respectively, THF being the eluent. The elution rate was 1 cm^3 min^{-1}, the concentration of injected samples was *ca* 0.4% w/w. Under these conditions the i.r. detector setting was 16x and 18x, respectively while u.v. detector was set to 4x.

The calibration curves were obtained experimentally using the Waters Associates standards possessing molecular weight ranging from 1900–2 700 000.

The products of combination were considered as being pure homopolymers from the point of view of molecular weights examined. This assumption seems plausible since there is only a small contribution of the combining component to the whole macromolecule. Moreover, the values of $\langle \bar{r}_0^2 \rangle$ (unperturbed end-to-end distance) for polystyrene, polydimethylsiloxane and tetrahydrofuran are similar.

RESULTS AND DISCUSSION

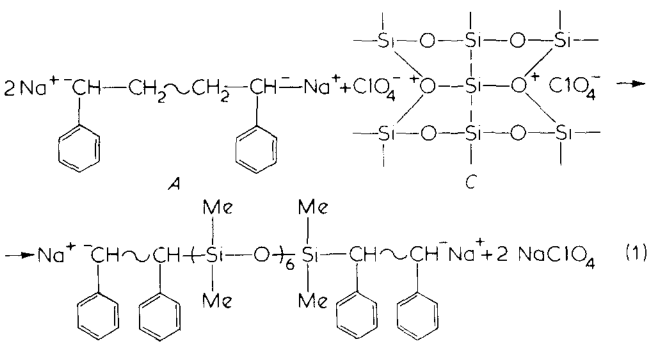
The interaction of polystyrene dianion solution with the silenium dication is accompanied by macroscopic clearly visible changes in the system:

(1) Viscosity increases almost instantly. Although the solution becomes less viscous after several hours, the resulting viscosity is always higher than before the combination.

(2) When the components are combined at 298K the colouration of carbanions disappears very quickly. This phenomenon may be observed even when the dication is present at a considerably lower concentration than dianion.

When the temperature of combination is below 233K the solution remains red for a long time even at significant excess of dication. The rate of discolouration will depend upon the ratio of dianion to dication ($[A]/[C]$). At $[A]/[C]$ = 0.8 the time required for a complete discolouration is more than 10 hours.

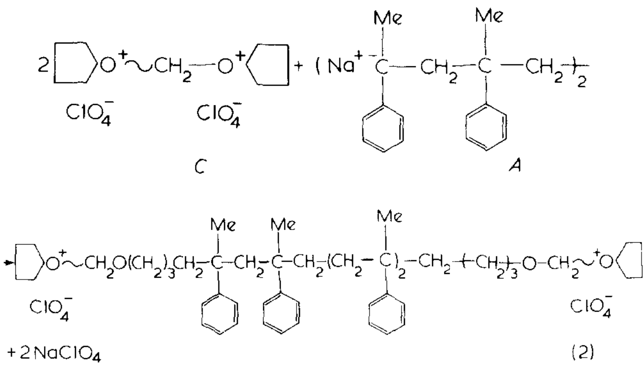
It seems that during the interaction polystyrene blocks are bonded together via siloxane links:



(1)

Curves in *Figure 3* illustrate a dramatic increase of the molecular weight of product with a maximum at $[A]/[C] \sim 0.95$. It is obvious that those ions which are in excess will be bonded to macromolecular ends. A similar situation has already been described for the case of polycondensation[19]. The product polydispersity remains practically constant (2.7 ± 0.2) over the studied range of $[A]/[C]$ ratios. There is only a slight increase when the molecular weight of dianion ($\bar{M}_A$) is raised (see *Figure 4*). The temperature of combination has almost no influence upon the polydispersity coefficient (D).

Yamashita *et al.*[4] have pointed out the possibility of a pronounced decrease of a number of combinations per one block copolymer which might be due to $H^{\ominus}$ and $H^{\oplus}$ elimination or due to proton transfer. The elimination of $H^{\ominus}$ is quite possible in our case; the reaction connected with the change of $H^{\oplus}$ or $CH_3^{\oplus}$ position is, however, very unlikely in the case of silenium cation. Such an undesirable process could take place during the interaction of a carbocation (carboxonium ion) with a carbanion. Therefore, we have examined the changes of molecular weight of living PTHF whose cationic ends were given the opportunity to react with the carbanion of living α-methylstyrene tetramer:



(2)

Figure 5 shows again the dependence of product molecula weight upon the $[A]/[C]$ ratio. The polydispersity coefficient varies but no pronounced tendency was observed when changing $[A]/[C]$ ratio. Its value is somewhat higher than in the previous case (2.9 – 3.5). This is probably due to the presence of low molecular macrocycles in PTHF[12]. Neither

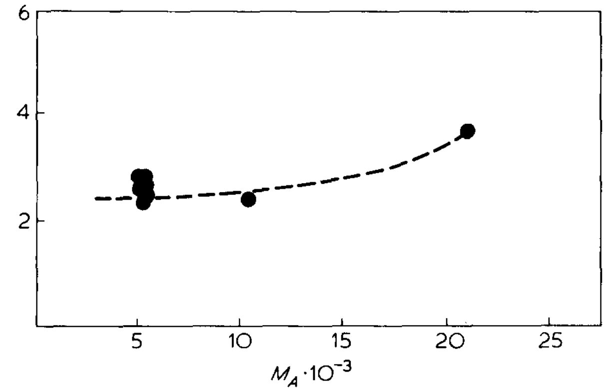


Figure 4 Dependence of polydispersity coefficient on molecular weight of dianion

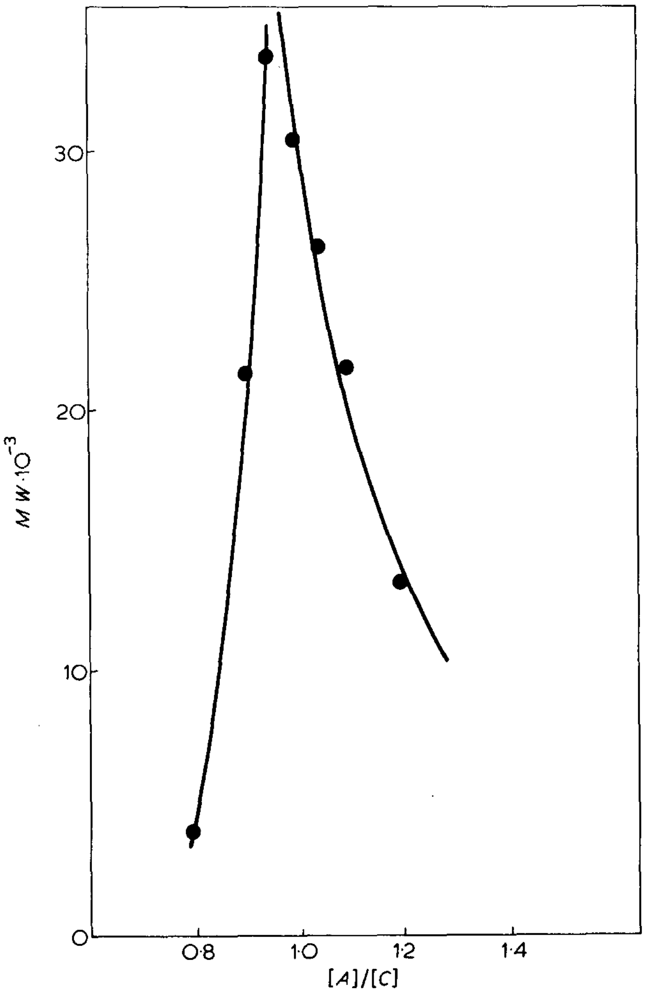


Figure 5 Dependence of molecular weight on ratio of dianion to dication. Temperature of THF polymerization and combination 263 K; A Na,⁻[α-MeS tetramer] $^{\ominus}$, Na$^{\oplus}$; C = PTHF dication; $\bar{M}_C$ = 1300–1600

variations of dication molecular weight ($\bar{M}_C$) over the interval 1300–37 000 exhibit significant influence upon the polydispersity coefficient.

It seems that in both cases the maximum efficinecy of combintion is achieved at a slight excess of dication (2–5%). This observation is, however, not very reliable; at [A]/[C] approaching unity the system becomes very sensitive and the possibility of experimental errors is high. The attempts to combine silenium and α-methylstyrene initiator diions were influenced negatively by this sensitivity. It was not possible to obtain a sufficiently homogeneous product. Even at 195K highly viscous mass was formed which contained siloxane and α-methylstyrene agglomerates. The experimental error was also high at combination where low molecular polymer component entered the reaction.

Although the scatter of experimental values is considerable and the error introduced by the presence of macrocycles in PTHF[12] is not negligible, the dependence of combination efficiency – represented by $\bar{P}_n$ of product (number of blocks) – on $\bar{M}_A$ or $\bar{M}_C$, may be approximated to assume an identical course. This is demonstrated in *Figure 6*.

The interaction of A and C is, in fact, polycondensation. Formally, this will obey the Carothers relationship[20]:

$$\bar{P}_n = \frac{1}{1-\frac{pf}{2}} \tag{3}$$

or

$$\sigma = \frac{1}{1-\frac{f_E}{2}} \tag{3a}$$

where σ stands for the number average degree of polymerization (in this case each of the combining diions is a 'monomer'), p represents a relative number of end groups which reacted and f is the average functionality of A and C, respectively. Because each ion either reacts to give the copolymer or is deactivated by a side reaction, the value of p may be regarded as being equal to unity. The relationship between f and $\bar{P}_n$ is shown in *Figure 7*. Experimental values σ_{max} then enabled the functionality f_E to be found. Comparison of f_E with the theoretical value (= 2.00) allowed the efficiency of combination to be calculated.

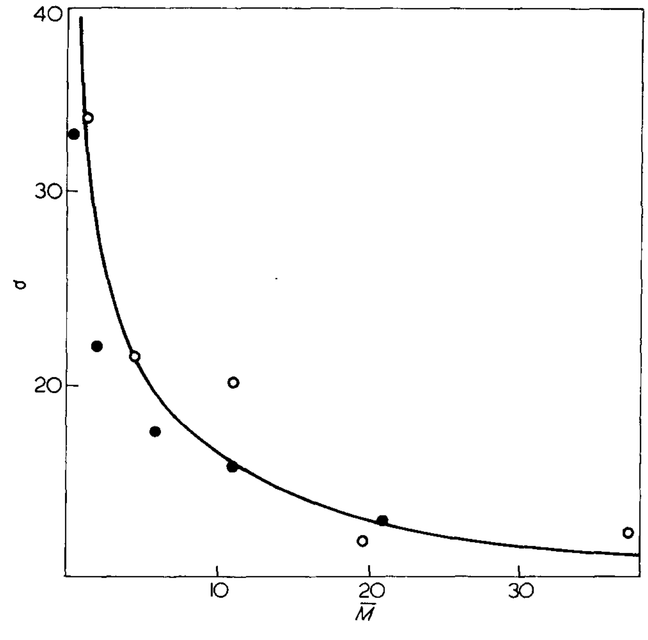


Figure 6 Dependence of number of blocks (σ) on $\bar{M}_C$ and $\bar{M}_A$ resp. at [A]/[C] = 1. (●), $^{\ominus}$PS$^{\ominus}$+ C (silenium initiator); (○), $^{\oplus}$PTHF$^{\oplus}$ + A ($^{\oplus}$Na, $^{\ominus}$[α-MeS tetramer]$^{\ominus}$, Na$^{\oplus}$)

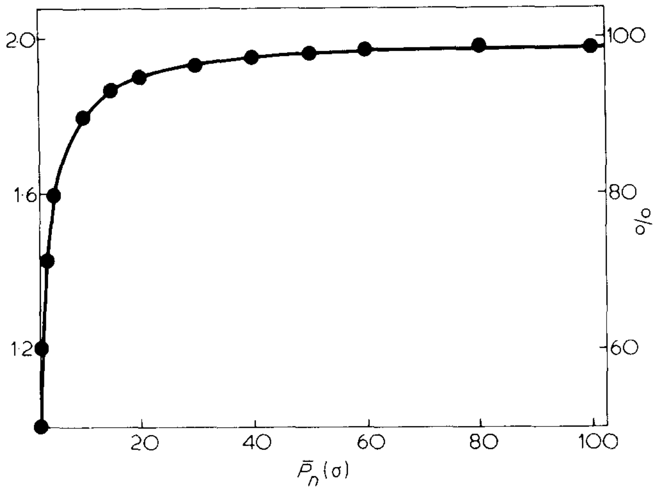


Figure 7 Correlation between functionality f and polymerization degree $\bar{P}_n$

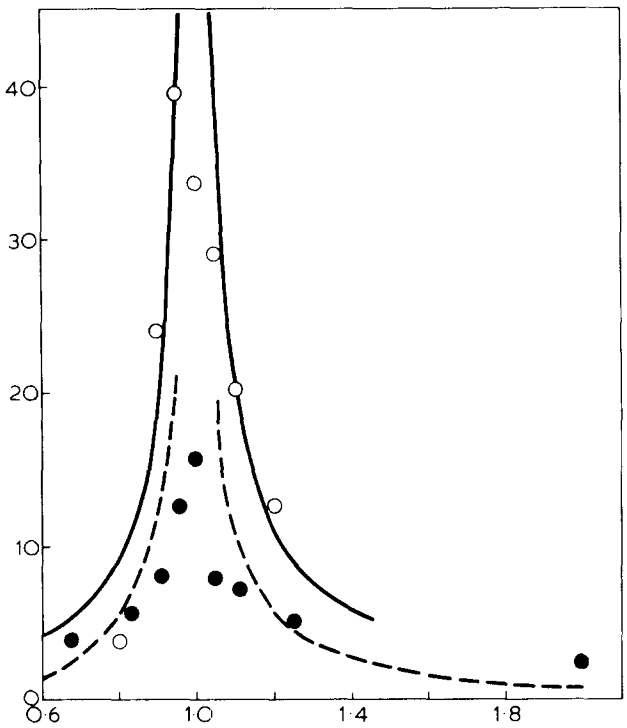


Figure 8 Polymerization degree (number of blocks) in the presence of excess of combining component (○), $^{\oplus}$PTHF$^{\oplus}$ and $^{\ominus}(\alpha$MeS$)_4^{\ominus}$; (●), $^{\ominus}$PS$^{\ominus}$ and $^{\oplus}$(Si-O)$_6$-Si$^{\oplus}$

The degree of polymerization for reactions (1) and (2) is a function of $\bar{M}_A$ and $\bar{M}_C$ (*Figure 6*):

$$\sigma = a\bar{M}_i^b \tag{4}$$

$\bar{M}_i$ denotes the molecular weight of polymer diion, either $\bar{M}_A$ or $\bar{M}_C$, a and b being constants. When the value of $\bar{M}_A$ and $\bar{M}_C$ is about 10^3 then f_E is found within 1.91–1.94 which corresponds to 95–97% efficiency. At $\bar{M}_A$ and $\bar{M}_C$ *ca* 35 x 10^3 the value of f_E decreases to 1.83 i.e. 91.5% efficiency. Such a high efficiency of combinations has already been observed by Richards *et al.*[18] in the case of polystyryldianion and polytetrahydrofuran dication.

The end groups in the product consist of the residual diions. The number of alternating combined diions in the macromolecule can be expressed as follows:

$$\sigma = \frac{[C] + [A]}{|[C] - [A]|} \tag{5}$$

The 'polymerization degree' calculated according to equation (5) was compared with the experimentally found number of alternating blocks (see *Figure 8*). Because the molecular weight of polystyrene component was higher in this case (5.6 x 10^3), the relationship (4) was taken into account. In both cases the results agree with previous measurements[12]. Values of a and b were found to be 221.4 and –0.275, respectively.

The combination of dianions with dications offers a number of novel possibilities in the field of polymer and copolymer synthesis. The present state of knowledge is indicative of a high efficiency of this reaction. There are also gaps in our knowledge which stimulate a series of questions. It seems that more work in this area will be necessary and useful.

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