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Sequence Distribution of Styrene Units in Poly(styrene-co-tetramethylene disulfide) Obtained from Chain Transfer Copolymerization

Manfred L. Hallensleben

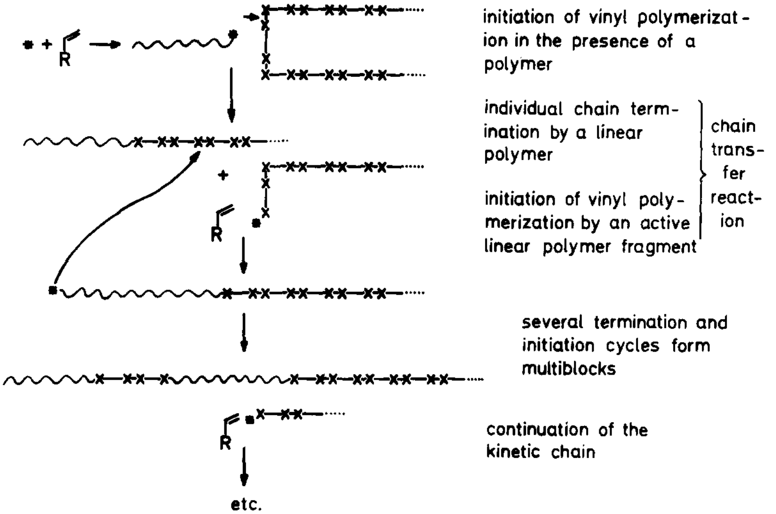
Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität,
Hermann-Staudinger-Haus, Stefan-Meier-Straße 31, 7800 Freiburg i. Br.,
Federal Republic of Germany

Synopsis

Copolymers obtained from radical styrene polymerization in the presence of poly(tetramethylene disulfide) were subjected to sulfur-sulfur bond cleavage by butyllithium. The resulting oligo- and poly(styrene) molecular weight distribution is identical with the sequence distribution of styrene sequences in the copolymer which proved to be a multiblock. From this, the apparent chain transfer constant of poly(tetramethylene disulfide) was calculated.

Introduction

The sulfur-sulfur bond in disulfides has been described as to react with carbon radicals under the formation of a new carbon-sulfur bond and a thiyl radical which, in the presence of a suitable monomer, proceeds to grow a new chain (HALLENSLEBEN 1976a). Our lab-



This scheme only holds if the eliminated polymer fragment is reactive enough to start a new chain

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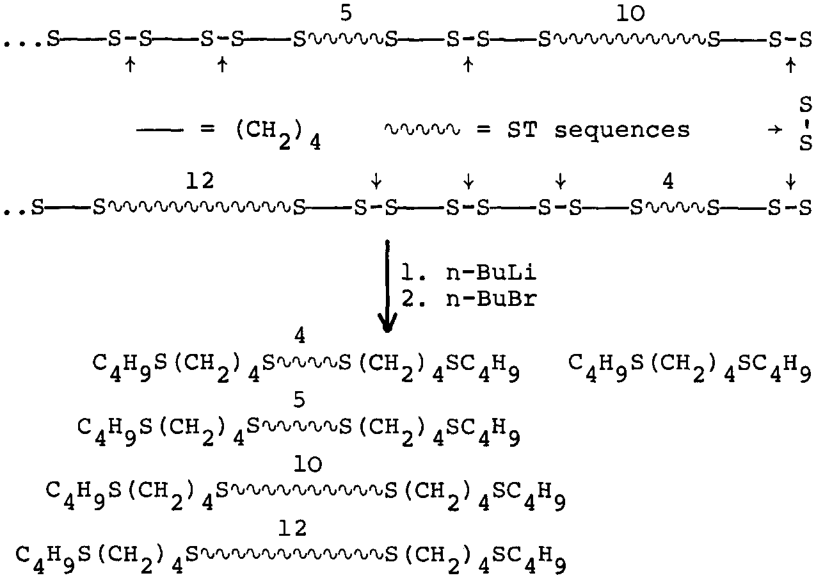
oratory has been able to show that this reaction opens a new route to obtain copolymers in such a way that a radical polymerization of a vinyl monomer, e.g., is carried out in the presence of a poly(disulfide), the sulfur-sulfur linkages of which act as the chain transferring moieties (STOCKMAYER et al. 1953, TOBOLSKY et al. 1953, HALLENSLEBEN 1976b, 1977). From the reaction scheme it becomes obvious that a copolymer once formed by a carbon radical attack upon a sulfur-sulfur bond in a poly(disulfide) molecule holds more active sites for the chain transfer reaction to proceed. Therefore broad chemical heterogeneity has to be expected for the copolymers since reaction of a growing polymer species with the chain transferring linkages of the prepolymer happens to occur randomly.

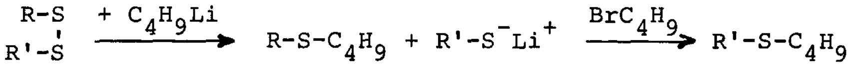
$$\frac{1}{P_n} = \frac{1}{P_n^o} + C_{tr} \cdot \frac{[Tr]}{[M]} \qquad 1$$

The MAYO equation **1** relates the degree of polymerization P_n with the chain transfer constant C_{tr} of a transfer agent Tr added to the polymerization system. In our case we get "P_n" of the polymerized vinyl monomer from cleaving all sulfur-sulfur bonds in the copolymer thus releasing the vinyl sequences which correspond to P_n of chain transfer polymerization with low molecular weight transfer agents. In this system "P_n" represents the vinyl sequence length in the copolymer.



Experimental

Radical chain transfer copolymerization experiments were carried out as described earlier (HALLENSLEBEN 1976b, 1977). MERCK butyllithium was used for the cleavage of the sulfur-sulfur bonds. The resulting Li-thiolate molecules were treated with 1-bromobutane in



$$\begin{array}{l}R\text{-}S\\ \;\;|\\ R'\text{-}S\end{array} \xrightarrow{+\,C_4H_9Li} R\text{-}S\text{-}C_4H_9 + R'\text{-}S^-Li^+ \xrightarrow{BrC_4H_9} R'\text{-}S\text{-}C_4H_9$$

order to get a simpler reaction product mixture. The cleavage mixture was extracted with methanol and after evaporation of the solvent the residual materials were identified by GC. From the methanol insoluble fraction GPC traces were recorded in THF at 293K and $\overline{M}_n$ was determined osmometrically. From the cleavage of the copolymer only two types of products were identified: 5,10-dithia tetradecane and oligo- and poly(styrene)s, respectively, of different molecular weight containing two $C_4H_9S(CH_2)_4S$- end groups. Concentration of oligo(styrene)s with initiator molecule end groups was too low as to be found and identified. Poly(tetramethylene disulfide) was prepared according to FIELD and BARBEE (1969) and had a $\overline{M}_n$(osm) of 3.100.

Results and Discussion

From the well established chain transfer mechanism from growing polymer chains to chain transfer moieties in a polymer backbone, three dominating questions arise challanging to be answered:

1) At a given chemical structure of the prepolymer and the active sites which play the role to re-initiate and propagate, what then is the amount of unipolymer at any given monomer conversion?

In the system under study, this question is answered by Figs.1 and 2. Up to 18% styrene monomer conversion no uni-poly(styrene) was found (Fig.1), but is present at higher monomer conversion with increasing number average molecular weight as conversion increases (Fig.2). That means that at low monomer conversion all growing chains are terminated by chain transfer to poly(tetramethylene disulfide) under copolymer formation by which process the number of sulfur-sulfur chain transfer linkages decreases. The experiments show that at the same time the amount of non-reacted poly(tetramethylene disulfide) drops fairly quickly at the beginning of styrene monomer consumption (Fig.1).

In previous investigations we had determined C_{tr} for dibutyl disulfide to be in the order of 10^{-2} (HALLENSLEBEN 1976a), and since even at a styrene monomer conversion of 18% with all hitherto grown chains term-

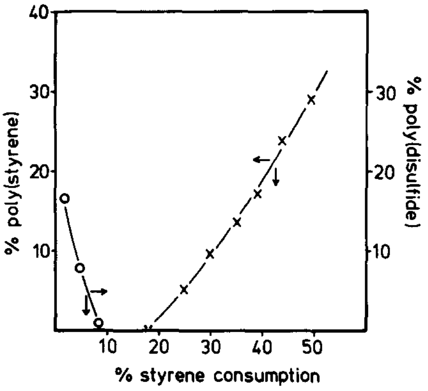


Fig.1 Unipolymers in chain transfer copolymerization of styrene with poly(tetramethylene disulfide)

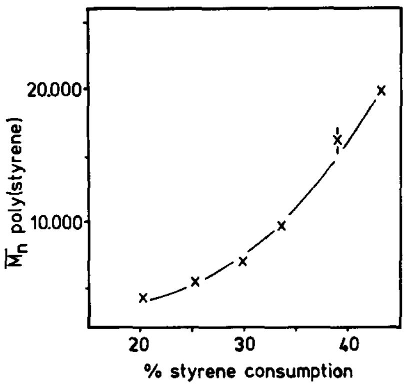


Fig.2 $\bar{M}_n$ of unipoly(styrene) formed

inated by the reaction with sulfur-sulfur bonds, the concentration of chain transfer linkages is still high enough as to be active according to the MAYO equation. The formation of uni-poly(styrene) therefore may derive from circumstances connected with a reduced accessibility of the sulfur-sulfur bonds in copolymer molecules.

2) Chain transfer from growing chains to polymer backbone linkages will happen to occur randomly; what, therefore, is the sequence length of the vinyl polymer sequences in the resulting multiblock from which C_{tr} of the sulfur-sulfur linkages can be derived?

Cleavage of all sulfur-sulfur bonds in the copolymer according the scheme above sets free the styrene sequences, the number average molecular weights of which were used as P_n to calculate C_{tr} from the MAYO equation. In this calculation from which the results are compiled in Tab.1, the change of sulfur-sulfur bond concentration during polymerization is negligable as becomes evident from experiment 3. At a styrene conversion of 25%, 5% uni-poly(styrene) is formed (see Fig.1), and P_n of styrene sequences in the copolymer is 40, so that the change of sulfur-sulfur bond concentration in the system is less than 2%. As becomes obvious running from 6% to 47% styrene monomer conversion, C_{tr} for poly(tetramethylene disulfide) changes by one order of magnitude which has nothing to do with the decrease of the concentration of the chain transfer moieties during polymerization, but may be attributable to the, perhaps, reduced accessibility of the sulfur-sulfur linkages for styrene radical chain ends to undergo chain transfer.

Table 1

Experiment	Styrene Conversion (%)	P_n^o a)	P_n	$C_{tr} \cdot 10^2$ from P_n
1	6	310	28	3,05
2	15	330	37	2,3
3	25	340	40	1,7
4	31	350	53	1,1
5	47	430	107	0,27

a) determined from individual experiments

$[Tr]_o = [M]_o = 0{,}2$ mole/l; AiBN; benzene; 338K

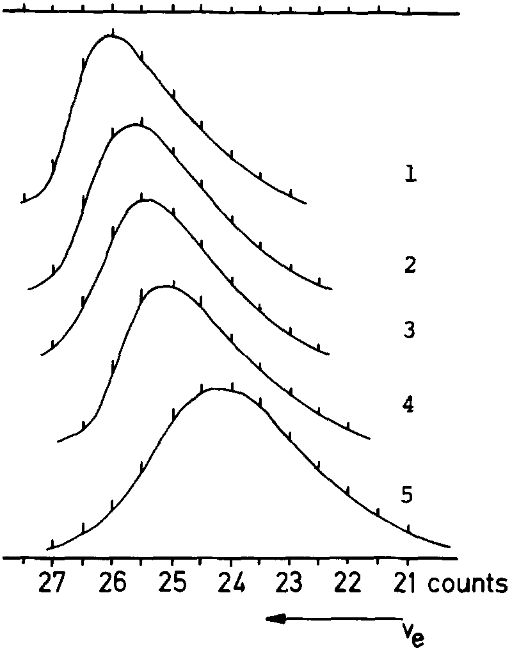


Fig.3 GPC traces of styrene blocks related to Tab.1

Fig.3 presents gel chromatograms of the styrene sequences from experiments 1 to 5 of Tab.1. With increasing styrene conversion a broadening of the elution curves is observed indicating that the statistics of individual chain termination by the chain transfer process at higher conversion is influenced by some other factors.

Determination of sequence distribution of the poly(tetramethylene disulfide) sequences in the copolymer will be presented in a forthcoming paper in this journal (HALLENSLEBEN, ZUGENMAIER).

3) A third question has to be discussed for fully to describe all processes: What influence does polymer conformation take on accessibility of the backbone linkages for active growing sites, in other words, to what extent do concentration of reactants, solvent, and temperature affect kinetics of copolymer formation and structure thereof?

C_{tr} actually is the ratio of the rate constants k_{tr} and k_p which, for radical polymerization processes, not very much depend on the polarity of the solvent, but they both do for ionic polymerization reactions which also can be used for chain transfer copolymerization (DZHAVADYAN et al. 1972, FRITZ et al. 1978). We therefore ascribe the decrease of C_{tr} in Tab.1 with increasing styrene conversion to polymer to influences of the accessibility of the chain transfer linkages to growing radical chains.
These problems are under investigation.

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