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Chain transfer constants of some alipathic agents in the polymerization of styrene and methylmethacrylate

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Summary

The chain transfer constants of various aliphatic compounds in the free radical polymerization of styrene and methyl methacrylate have been determined at 60^0C. It has been found that some cycloaliphatic compounds show a remarkable chain transfer activity, which can also be of practical interest.

Introduction

In polymer chemistry chain transfer is a process where a polymerizing free radical removes an atom from another molecule, forming an inactive polymer and a new radical. The ratio of the rate constants of a transfer reaction and the normal addition of the monomer is called the transfer constant (1) and measures the relative reactivity of the growing radical toward the transfer substance.

The principle of chain transfer was introduced into the kinetics of polymerization by Flory (2) in 1937. First reports on the effect of chain transfer were given by Breitenbach (3) (1938) and Schulz et al. (4) (1939). Kinetic investigations of transfer reactions have been carried out in 1942 by Schulz and Blaschke (5). In 1947 Gregg and Mayo (6) studied the effect of solvents in the kinetics of transfer reactions.
In preliminary investigations (7) it was found, that some cyclohexan derivatives and similar aliphatic compounds show a remarkable chain transfer activity, which can be used in graft copolymerizations with respective monomer units. Therefore, in the present study, we will report on the effect of various aliphatic compounds on the free radical polymerization of styrene and methyl methacrylate.

Compounds

The following substances were used for the investigations of their chain

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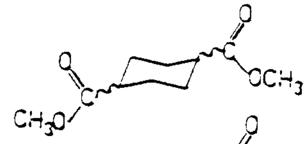
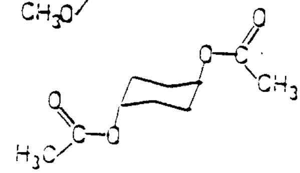
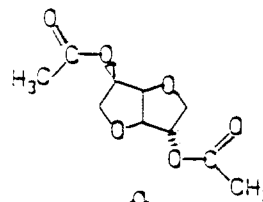
cis/trans-1,4-cyclohexandicarboxylic acid dimethylester



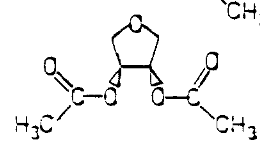
trans-1,4-cyclohexandiacetate



1,4:3,6-dianhydrosorbit-2,5-diacetate



cis-3,4-diacetoxyoxolane



Theoretical

The transfer constant for an uncatalysed polymerization, C_T, is given by Equation 1

$$1/P_n = 1/P_{n,o} + C_T\,[T]/[M] \qquad \text{Equation 1}$$

where P_n is the number average degree of polymerization formed in the presence of a transfer substance [T] at a monomer concentration [M]; $P_{n,o}$ is the number average degree of polymerization in absence of the transfer substance.

In general case the monomer (M), the initiator (I), an added transfer substance (T) or the growing polymer (P) can operate as a chain transfer agent (6):

$$1/P_n = 1/P_{n,o} + C_M + C_I[I]/[M] + C_T[T]/[M] + C_P[P]/[M] \qquad \text{Equation 2}$$

C_M = transfer constant of the monomer M
C_I = transfer constant of the initiator I
C_T = transfer constant of the transfer agent
C_P = transfer constant of the polymer P

The transfer constant of most polymers C_P and C_I for benzoyl peroxide initiated polymerizations is very small. Hence if [I]/[M] is kept constant Equation 2 can be written as (8-10):

$$1/P_n = 1/P_{n,o} + K + C_T[T]/[M] \qquad \text{Equation 3}$$

with

$$K = C_M + C_I[I]/[M] + C_P[P]/[M] = \text{constant}$$

Results

The transfer constants were determined by variation of the ratio of the investigated compounds to monomers at 60°C in polymerization experiments at low conversions. The molecular weights of the polymers were obtained by gel permeation chromatography (GPC) and the results are shown in Table 1.

The transfer constants are calculated from the slopes of the straight lines obtained by plotting the reciprocal number average degree of polymerization against the ratio of transfer substance to monomer concentration.

An example for the determination of transfer constants is shown in Figure 1. The transfer constants (C_T) of the other substances were obtained in a similar way and are listed in Table 1.

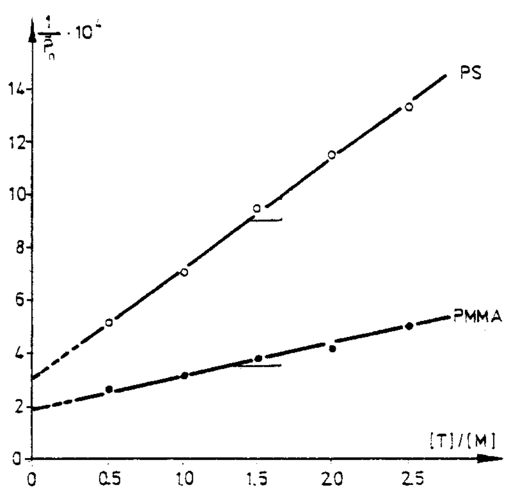


Figure 1. Determination of transfer constants of cis/trans-1,4-cyclohexan-dicarboxylic acid dimethylester in styrene and methyl methacrylate polymerization at 60°C.

Table 1. Transfer constants in styrene (a) and methyl methacrylate polymerization at 60°C with $6{,}06\cdot10^{-2}$ mol-% (to monomer) benzoyl peroxide; [M] = 0,05 mol.

transfer substance	[T]/[M]	M_n	$1/P_n\cdot10^4$	C_T
a) styrene				
cis/trans-1,4-cyclo-	0,5	202000	5,15	
hexandicarboxylic acid	1,06	146000	7,12	
dimethylester	1,5	110000	9,45	$4{,}2\cdot10^{-4}$
	2,0	90500	11,49	
	2,5	78000	13,33	
trans-1,4-cyclohexan-	0,025	140000	7,43	
diacetate	0,05	132000	7,88	
	0,075	125000	8,32	$1{,}69\cdot10^{-3}$
	0,1	117000	8,89	
	0,15	109500	9,5	
1,4:3,6-dianhydro-	0,025	184000	5,65	
sorbit-2,5-diacetate	0,05	129000	8,06	
	0,075	99000	10,51	$7{,}7\cdot10^{-3}$
	0,1	81000	12,84	
	0,15	69000	15,14	
cis-3,4-diacetoxy-	0,5	138000	7,54	
oxolane	1,0	123000	8,46	
	1,5	113000	9,2	$1{,}89\cdot10^{-4}$
	2,0	100000	10,4	
	2,5	91000	11,4	
b) methyl methacrylate				
cis/trans-1,4-cyclo-	0,5	382000	2,62	
hexandicarboxylic acid	1,06	309000	3,24	
dimethylester	1,5	264000	3,79	$1{,}16\cdot10^{-4}$
	2,0	238000	4,2	
	2,5	201000	4,96	
trans-1,4-cyclohexan-	0,025	510000	1,96	
diacetate	0,05	459000	2,18	
	0,075	422000	2,37	$8{,}46\cdot10^{-4}$
	0,1	380000	2,63	
	0,15	332000	3,01	
1,4:3,6-dianhydro-	0,025	595000	1,68	
sorbit-2,5-diacetate	0,05	403000	2,48	
	0,075	321000	3,13	$2{,}9\cdot10^{-3}$
	0,1	231000	4,33	
	0,15	192000	5,21	
cis-3,4-diacetoxy-	0,5	538000	1,86	
oxolane	1,0	348000	2,87	
	1,5	338000	2,96	$1{,}39\cdot10^{-4}$
	2,0	250000	4,0	
	2,5	210000	4,76	

Discussion

A comparison of the chain transfer effect of various substances leads to conclusions about the reactivity of polymer radicals and the bond strength of the transfer atoms in the transfer substances.

Transfer constants of solvents vary from $2 \cdot 10^{-6}$ for benzene (11) in the polymerization of styrene up to 5700 for carbon tetrabromide (11) in the polymerization of vinylacetate. Regulators are substances with high transfer constants, e.g. mercaptans, which are very suitable for the regulation of molecular weights; their transfer constants (11) are in the range of 10^{-1} to 10^{1}.

The transfer constants of cis/trans-1,4-cyclohexandicarboxylic acid dimethylester and cis-3,4-diacetoxyoxolane in the styrene polymerization are similar to those of acetone ($4,1 \cdot 10^{-4}$), 1,2-dichlorethane ($4,12 \cdot 10^{-4}$) and diphenylmethane ($2,3 \cdot 10^{-4}$) and in the methyl methacrylate polymerization with those of benzaldehyde ($2,5 \cdot 10^{-4}$), carbon tetrachloride ($0,925 \cdot 10^{-4}$) and chloroform ($1,77 \cdot 10^{-4}$). The transfer constant of trans-1,4-cyclohexandiacetate in the polymerization of styrene is similar to those of dibutylsulfide ($2,2 \cdot 10^{-3}$), dibutyldisulfide ($2,4 \cdot 10^{-3}$) and dibenzylsulfide ($3,35 \cdot 10^{-3}$). Those of 1,4:3,6-dianhydrosorbit-2,5-diacetate in the styrene polymerization is comparable with diphenylsulfide ($5,48 \cdot 10^{-3}$), diphenyldisulfide ($8,78 \cdot 10^{-3}$) and dimethyldisulfide ($9,4 \cdot 10^{-3}$). The transfer constants of both model compounds in the polymerization of methyl methacrylate can be arranged in the series of diphenyldisulfide ($7 \cdot 10^{-4}$), diphenylsulfide ($1,54 \cdot 10^{-3}$) and dibenzyldisulfide ($6,27 \cdot 10^{-3}$).

The transfer constants of the compared substances are taken from the literature (11).

Experimental

Benzoyl peroxide was recrystallized and dried. Styrene and methyl methacrylate were freed from inhibitor, dried and distilled under reduced pressure in dry nitrogen shortly before use.

Cis/trans-1,4-cyclohexandicarboxylic acid dimethylester

Cis/trans-1,4-cyclohexandicarboxylic acid dimethylester (50:50) (Merck) was purified by distillation (b.p.: 132°C/20 mbar).

Trans-1,4-cyclohexandiacetate

A solution of 100 g (0,86 mol) cis/trans-1,4-cyclohexandiole, 500 g (5,56 mol) acetic anhydride and 1 g p-toluenesulfonic acid was refluxed for 4 h. The excess of acetic acid and acetic anhydride was removed by vacuum distillation. The mixture of cis and trans diacetate was distilled under reduced pressure by 116°C and 20 mbar. (Ref. (12): m.p.: 101°C, b.p.: 116-118°C/20 mbar).

The trans isomer was separated by recrystallizing the acetyl derivative in acetone at 0°C.
Purification was done by crystallizing in hot anhydrous methanol.
Yield: 60 g (35 %); m.p.: 101°C (Ref. (12): 103°C).

1,4:3,6-Dianhydrosorbit-2,5-diacetate

A solution of 10 g (0,07 mol) 1,4:3,6-dianhydrosorbit, 10 g sodium acetate and 30 ml acetic anhydride was refluxed for 1,5 h. The cooled mixture was poured into ice water and the treacle crystallized slowly.
The product was filtered and recrystallized in ethanol.
Yield: 14,64 g (91%); m.p.: 61°C (Ref. (13): 60-61°C).

Cis-3,4-diacetoxyoxolane

10 g (0.096 mol) of 1,4-anhydroerythritol were dissolved in 50 g (0,48 mol) acetic anhydride and refluxed with 0,1 g p-toluenesulfonic acid for 4 h. The mixture was distilled under reduced pressure.
Yield: 15 g (83 %); $b.p._{0,5}$: 80°C (Ref. (14): 79-81°C/0,53 mbar).

Polymerization

Mixtures of redistilled monomers, model compound and the initiator, benzoyl peroxide, were transferred into reaction tubes with the desired ratio of [T]/[M] and degassed. Then the reaction tubes were heated in a thermostat at 60°C until about 10 % conversion was obtained. The polymers were isolated by precipitation in methanol (polystyrene) and pentane (polymethyl methacrylate).

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