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Reactions

Oligomers of α-methylstyrene by initiation with tetraphenylethanes*

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Summary

With substituted tetraphenylethanes as polymerization initiators, telechelic oligomers of α -methylstyrene were obtained above ceiling temperature, contrary so far to other free radical reactions using e.g. chain transfer agents. In the here investigated system tetraphenylethanes act as initiators and terminating agents. The C-C bond between the last monomer unit of the oligomer and the terminating end group from the initiator can be thermally cleaved at about 50°C which produces free radcials. Thus, these α -methylstyrene oligomers can be applied as initiators of free-radical polymerization, e.g. for styrene or methyl methacrylate.

Introduction

Several reports on the chemically - initiated polymerization of α - methylstyrene have been published (1). Polymerization in an electric field has been studied (2,3). Electroinitiated anionic polymerization of α-methylstyrene has been reported by Yamazaki et al. (4) and cationic polymerization by Akbulut et al. (5).

Also the oligomerization of α-methylstyrene has been studied extensively. The cationic polymerization of α-methylstyrene by binary metal oxides at 30°C yields oligomers, especially dimers and trimers, as major products (6,7). There are two different active sites which give olefin oligomers and indan ring containing oligomers. Radiation - induced oligomerization of α -methylstyrene, proceeding according to a cationic mechanisms, occurs only when the monomer was rigorously dried. The molecular weight of the polymers produced decreased with increasing temperature and oligomers are produced at high temperatures (8). Low molecular weight oligomers (dimer, trimer, tetramer) are predominantly produced above the ceiling temperature of the monomer (61°C). Products with unsaturated end group were not detected what indicates that at high temperatures cyclization of the propagating cation occurs in preference to direct β-proton transfer to monomer.

Also the radical oligomerization of α-methylstyrene was carried out at 50-90°C using bromotrichloromethane as a chain transfer agent (9). The ten isolated oligomers corresponding to n - mers with n = 1 - 3 had unsaturated or cyclic structures. Telomers containing bromine were not observed. This and other reports (10) show that during the initiation and termination step of the free radical polymerization of α-methylstyrene, a variety of polymer

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end groups can be generated due to different reactions of the initiator - derived radicals. The nature of these end groups is of significant influence on the chemistry of the resulting polymers. Reactive end groups may be desirable as sites for crosslinking and for producing functionalized polymers. The minimization of the number of end groups with double bonds increases the chemical stability of such polymers.

Poly(α-methylstyrene) seems to be a useful modifier as a flow promotor and melt viscosity depressant, reinforcing agent and solid plasticizer(11). In the present study the free radical oligomerization of α-methylstyrene at 90°C has been investigated. The obtained telechelic oligomers can be used as initiators for the polymerization of vinyl monomers.

Experimental

The synthesis of tetraphenylethane initiators was described in our previous papers (12):
TPPA 1,1,2,2 - tetraphenyl -1,2-diphenoxyethane,
TPCA 1,1,2,2 - tetraphenyl -1,2-dicyanoethane.

Synthesis of α -methylstyrene oligomers

TPPA - oligomers: commercial α-methylstyrene was purifed by the usual method and dried over calcium hydride. A 50 ml polymerization tube was shaked with 20 ml of α-methylstyrene and 2 g of TPPA in nitrogen atmosphere at 90°C. After 3 h the reaction mixture was added dropwise to 600 ml vigorously stirred methanol. No precipitate was observed. The methanol solution was then distilled under reduced pressure at 35°C and the remaining 1,80 g of white powder were dried in vacuo at 40°C.

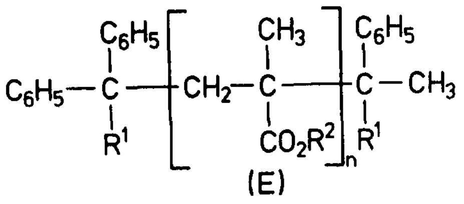
TPCA-oligomers: this reaction was performed in the same way. 20 ml of α-methylstyrene and 0,63 g TPCA gave 0,22 g oligomers.

Gel permeation chromatography: the distribution of the oligomers was determined with a Waters - system (pump model 510, refractometer R 401), UV-spectrometer LC-55 from Perkin-Elmer and six columns (30 cm, Ø8 mm) packed with 100 Å and 500 Å μ-Styragel and 100 Å, 2 x 500 Å and 10^4 Å Ultrastyragel at 30°C, 80 bar in THF. Thin layer chromatography was performed on DC-Al-plates with Kieselgel 60 F 254 from Merck with pentane/tetrahydrofurane = 95 : 5 (Vol.), 1 hour.

Field desorption mass spectrometry: Spectrometer MAT 311 A from Varian (pressure 10^{-6} mbar, potential of emitter 6 kV, 3 kV) with Oscillofil-recorder. The measurements were carried out from 0 to 15mA.

Results and discussion

Recently (12) the polymerization of methacrylic monomers using some 1,1,2,2-tetraphenylethanes as radical initiators was investigated and an unusual polymerization mechanisms, sometimes called "living free radical polymerization" (13) could be proved. This polymerization process is characterized by three steps: during the initial period oligomers from methacrylic monomer and initiator radicals are formed by primary radical termination:



$$C_6H_5-\underset{R^1}{\overset{C_6H_5}{C}}-\left[CH_2-\underset{CO_2R^2}{\overset{CH_3}{C}}\right]_n-\underset{R^1}{\overset{C_6H_5}{C}}-CH_3 \qquad (I)$$

$R^1 = OC_6H_5, CN, OSi(CH_3)_3$

$R^2 = H, CH_3, C_4H_9, C_6H_5CH_2$

These oligomers (I) produce free macroradicals and initiator radicals by cleavage of the bonds between the last monomer unit and the terminating end group from the initiator (E). Finally, after consumption of the initiator radicals with increasing conversion the normal propagation and termination processes occur. Contrary to methyl methacrylate, the styrene polymerization with the same 1,1,2,2-tetraphenylethanes occurs according to a different mechanism (14). In this case C-C-bonds between the last styrene unit and the terminating end group from the initiator are not cleaved at the usual polymerization temperature (50-100°C). Therefore this reaction can be described as a dead-end-polymerization.

For the polymerization of α -methylstyrene it could be expected that the C-C-bond between the last monomer unit and the terminating end group should be cleaveable analogously to methacrylic oligomers.

Oligomers of α -methylstyene and tetraphenylethane

Oligomers of α -methylstyrene were obtained in a similar way as methyl methacrylate (MMA) and styrene oligomers (12,14). Synthesis carried out at 60°C, i.e. little below the ceiling temperature, did not give the expected results. At such temperatures the central C-C-bond of the initiator is relativle stable resulting in small concentrations of primary radicals in the solution. Thus, the eventual polymerization (oligomerization) reaction proceeds very slowly. However, at 90°C considerable amounts of products, identified as α -methylstyrene oligomers, resulting from the competetive reactions of propagation, depolymerization and termination, were obtained.

Elementary analysis of oligomers obtained TPPA showed that the average molecular weight amounts to 1,5 assuming the presence of the initiator-derived radicals at both ends of the oligomer chain. Thin layer analysis showed the presence of several products. (Fig. 1).

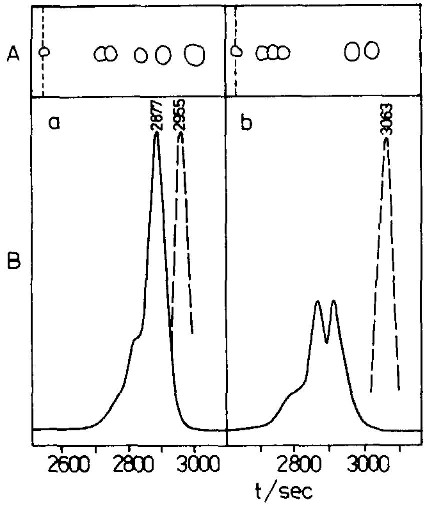


Fig. 1.
Thin layer (A) and gel permeation(B) chromatograms of α -methylstyrene oligomers: a) with TPPA; b) with TPCA
---initiator peak

Similary to the previously analyzed MMA and styrene oligomers (14) a distinct influence of the end group from the initiator on the separation effect is observed. Also the gel permeation chromatography showed the presence of only the first members of the homologuos series of both kinds of α -methylstyrene oligomers obtained. Yet, the lack of suitable standards precluded unmistakable identification of the components solely by chromatographic methods. Explicit identification of the investigated oligomers and confirmation of the presence of the end groups originating from the initiator at both ends of the chain were achieved by field desorption mass spectrometry. In the spectra of oligomers obtained from α-methylstyrene using TPCA as an initiator, a series which can be described by the relationship "192 + 118 n" has been found (Fig. 2).

The presence of the compound of "384 + 118" molecular weight has also been stated. From the fact that the molecular weight of the initiator equals 384 and that of the α-methylstyrene mer is 118 it results that the investigated oligomers were in fact initiated and terminated by primary radicals.

The spectrum was obtained at 12 mA, i.e. at relatively high emitter temperature, considerably exceeding 100°C, causing the cleavage of the terminal C-C bond under measurement conditions to a far higher degree than it has been stated for analogous styrene oligomers under the same conditions (Fig. 2).

Thus, the FD-MS analysis confirmed both the presence of only the first members of homologous series of oligomers and the fact that the terminal and C-C bond in the case of α -methylstyrene oligomers is far more labile than in the case of styrene oligomers. That is undoubtly caused by the presence of the methyl group as an additional substituent at the last monomer unit. Similar effects were observed previously for MMA oligomers (12).

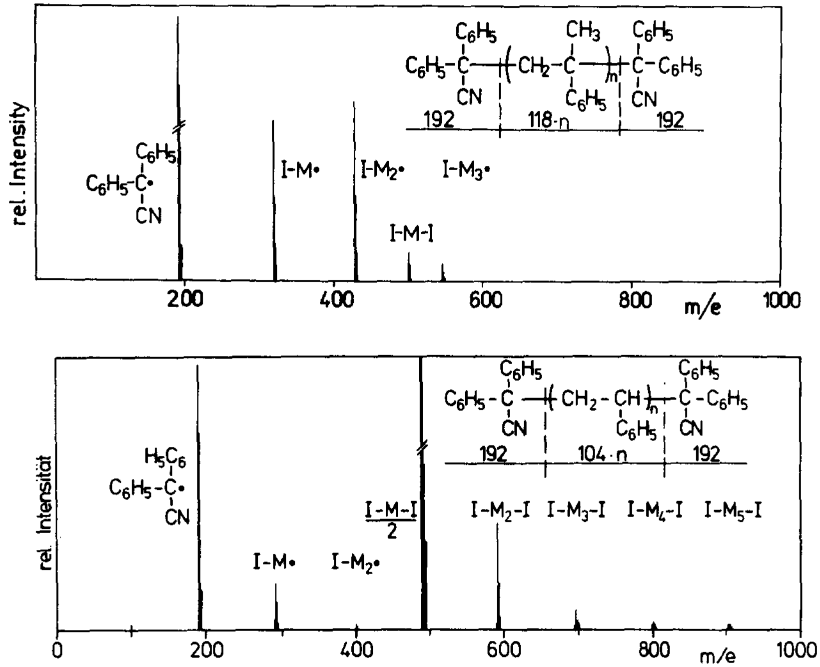


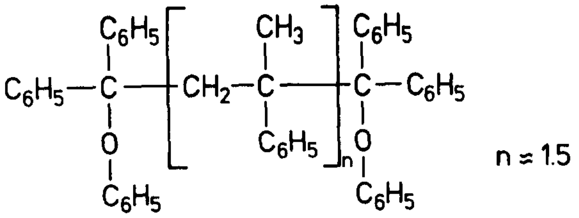
Fig. 2. Field desorption mass spectra at 12 mA of oligomers prepared with TPCA at 90°C

a) Oligomers of α-methylstyrene

b) Oligomers of styrene

Oligomers of α-methylstyrene as radical initiators

Oligomers of α-methylstyrene (II) of the following formula:



$$C_6H_5-C(C_6H_5)(O-C_6H_5)-\left[CH_2-C(CH_3)(C_6H_5)\right]_n-C(C_6H_5)(O-C_6H_5)-C_6H_5 \qquad n \approx 1.5$$

(II)

obtained using TPPA were applied for the initiation of the vinyl monomer polymerization (Fig. 3).

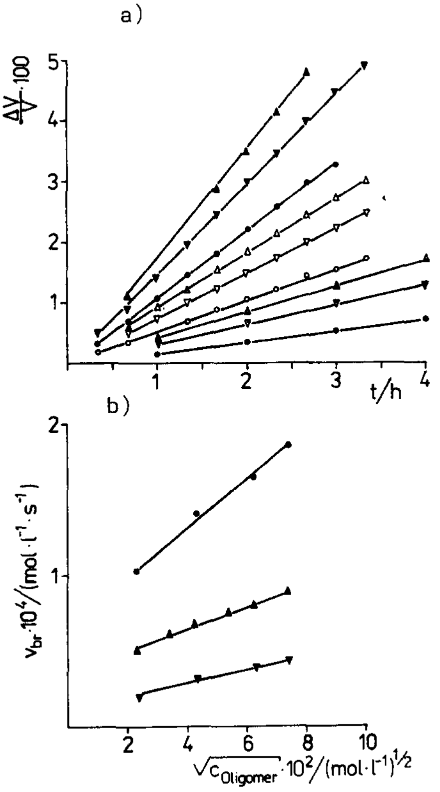


Fig. 3.
Polymerization of methyl methacrylate initiated with α-methylstyrene oligomers II
a) dilatometric time - conversion - dependence at 50°C (◐ ▼ ▲) 60°C(○ ▽ △), 70°C (● ▼ ▲) with different initiator concentrations ● 0,56, ▼ 1,86, ▲ 5,45 $\cdot 10^{-3}$ mol $\cdot$ l^{-1}
b) dependence of the rate of polymerization v_{br} of MMA on the square root of the initiator concentration at ▼ 50°C, ▲ 60°C, ● 70°C.

Dilatometric measurements confirmed considerable polymerization at already 50°C. Depending on the initiator concentration and temperature, different slopes of linear time - conversion relationships were obtained.

A similar dependence was previously stated for analogous oligomers obtained from MMA using TPPA (12). However, styrene oligomers having the same end groups did not show any ability for initiation of vinyl polymerization in the investigated temperature range. The rate of MMA polymerization shows a linear dependence on the square root of the initiator concentration (Fig.3), characteristic for typical free-radical polymerizations.

However, the styrene polymerization by these oligomers occurs in a different manner (Fig. 4), its rate is decreasing with the time, similary

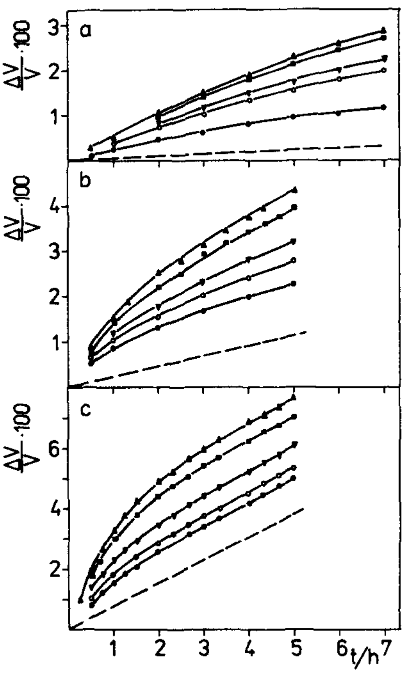


Fig. 4.
Dilatometric investigation of the styrene polymerization initiated with α-methylstyrene oligomers I at different temperatures:
a) 70°C; b) 90°C; c) 110°C
and initiator concentrations:
◆ 0,56; ○ 1,20; ▼ 1,86; ■ 3,39; △ $5{,}45\cdot10^{-3}$ $\text{mol}\cdot\text{l}^{-1}$
---without initiator

to the styrene polymerization initiated by various tetraphenylethanes. That confirms the dead-end type of styrene polymerization with this type of initiator. Comparison of the polymerization of MMA and styrene initiated by TPPA (n = 0) and by oligomers (n = 1,5) of α-methylstyrene using TPPA under analogous conditions of concentrations and temperature (Fig. 5) allows the general statement that the terminal C-C bond in these α-methylstyrene oligomers between the last monomer unit and the initiator - derived radical is very labile, cleaving at already 50°C and resulting in faster progress of the polymerization than in the case of TPPA, where a typical "three-period" polymerization is observed (12). Under analogous conditions the styrene polymerization rate is many times slower.

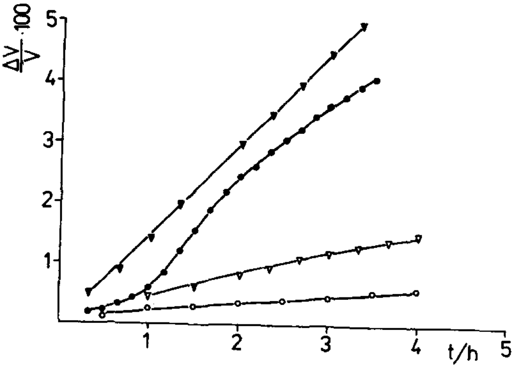


Fig. 5
Dilatometric investigations of styrene (▽ ○) and methyl methacrylate (▼ ●) polymerizations at 70°C initiated with TPPA (● ○) and α-methylstyrene oligomers (▼ ▽)

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References

1. J.P. Kennedy, R.T. Chou, J. Macromol. Sci. Chem. A 18, 11, 17, 47, 77 (1982)

2. I. Sakurada, N. Ise, T. Ashida, Makromol. Chem. 82, 284 (1965), 95, 1 (1966)

3. I. Sakurada, Y. Tanaka, N. Ise, J. Polym. Sci. A-1, 6, 1463 (1968)

4. N. Yamazaki, S. Nakahama, S.J. Kambara, J. Polym. Sci. , Polym. Lett. 3, 57 (1965)

5. U. Akbulut, S. Eren, L.K. Toppare, Polymer 25, 1028 (1984)

6. Y. Kawakami, N. Toyoshima, Y. Yamashita, Chem. Lett., 13 (1980)

7. Y. Kawakami, N. Toyoshima, T. Ando, Y. Yamashita, Polym. J., 13, 947 (1981)

8 Y. Yamamoto, M. Miki, K. Hayashi, Macromolecules 14, 208 (1981)

9. T. Kimura, M. Hamashima, Kobunshi Ronbunshu(Chemistry of High Polymers) 40, 773 (1983)

10. R.D. Grant, E. Rizzardo, D.H. Solomon, Makromol. Chem. 185, 1809 (1984)

11. V.V. Raimondi, A.P. Wilson, Society of Plastics Engineers, 42th Annual Technical Conference "Antec 84", 247 (1984)

12. A. Błedzki, D. Braun, et al., Makromol. Chem. 182, 1047, 1057, 1063, 3195 (1981), 184, 287, 745 (1983)

13. T. Otsu, M. Yoshide, Makromol. Chem., Rapid Commun. 3, 127 (1982)

14. A. Błedzki, D. Braun, Makromol. Chem., in press

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