Copolymerization of MMA and Methyl α-Phenylacrylate by GTP

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ABSTRACT: The copolymerization of MMA **(1)** and methyl α-phenylacrylate **(2)** by GTP has been studied. While no homopolymer could be obtained from **2**, alternating copolymers were formed from mixtures of **1** and **2**. Monomer consumption as measured by gas chromatography proved equimolar incorporation even with **1** in excess as long as **2** was present in the reaction mixture. MALDI−TOF mass spectrometry showed that all polymer chains contained **2** incorporated as first and last monomer resulting in a homologous series **Init.**(**2**,**1**)$_n$**2**. The propagation constants decrease in the order $k_{12} >> k_{11} > k_{21} >> k_{22}$. In model reactions of catalyst, ketene acetal, and **2**, 2-fold addition of **2** also occurred to a small extent. This is the origin of a second homologous series in the mass spectra of the alternating copolymers. Block copolymers with an alternating (**1,2**) block and a PMMA block are formed from a monomer feed having MMA in excess.

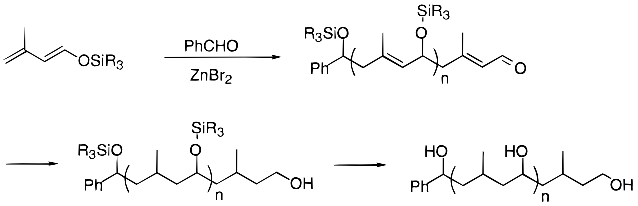
Introduction

Group transfer polymerization of acrylate- and methacrylate-based monomers has found widespread academic as well as industrial interest since its discovery in 1983.[1−4] Besides the Michael type polymerization, aldol group transfer polymerization of silyl enol ethers with aromatic aldehydes as initiators and Lewis acids as catalysts has been reported.[5,6] Block copolymers obtained by consecutive polymerization and random copolymerization of methacrylates with similar chemical constitution have been described.[7]

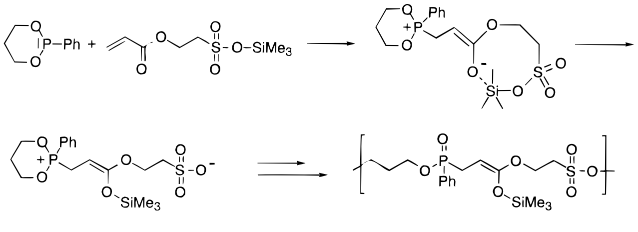
Two types of alternating copolymers in connection with group transfer polymerization have been reported in the literature. Sogah et al.[8,9] and Yokota et al.[10] polymerized 1-trimethylsiloxy 1,3-dienes by aldol-GTP, which proceeds via 3,4- and 1,4-addition depending on the structure of the diene. The polymer resulting after hydrogenation and desilylation had the structure of an alternating polymer of an α-olefin and vinyl alcohol, though it is a homopolymer as far as the synthesis is concerned (Scheme 1).

A second example has been reported by Kobayashi et al.[11,12] They used 2-phenyl-1,3,2-dioxaphosphorinane and 2-(trimethylsiloxysulfonyl)ethyl acrylate for zwitterionic polymerization and obtained an alternating copolymer containing silyl ketene acetal moieties in the repeat unit (Scheme 2). The mechanism of this reaction, however, is completely different from the GTP of acrylates. The silyl group transfer occurs from the sulfonate or carboxylate to the enolate, and a more stable anion is formed, which probably is the driving force of this reaction. Although this reaction is a real example of group transfer and the resulting polymer structure requires this transfer, it has nothing in common with the (meth)acrylate GTP as the ketene acetal is not involved in the propagation or in the stabilization of the active center.

Scheme 1



Scheme 2



True alternating copolymers by direct simultaneous group transfer polymerization of two different monomers have not been described up to now to our knowledge. Taking into account the structural requirements of monomers amenable to GTP, suitable monomers should have the structure of α-substituted acrylate esters. Copolymerization of methyl methacrylate and methyl α-phenylacrylate is one of the rare examples of an alternating copolymer obtained by anionic polymerization.[13] The alternating structure has been explained as due to the low ceiling temperature of poly(methyl α-phenylacrylate).

The work presented in this paper deals with the copolymerization of methyl methacrylate and methyl α-phenylacrylate by group transfer polymerization and elucidation of the mechanism by MALDI−TOF mass spectrometry.

Results

Monomers. Methyl α-phenylacrylate **(2)** was synthesized from methyl phenylacetate, dimethyl oxalate and formaldehyde according to the procedure of Ames and Davey[14] as outlined in Scheme 3. Methyl phenylacetate is reacted with dimethyl oxalate in the presence

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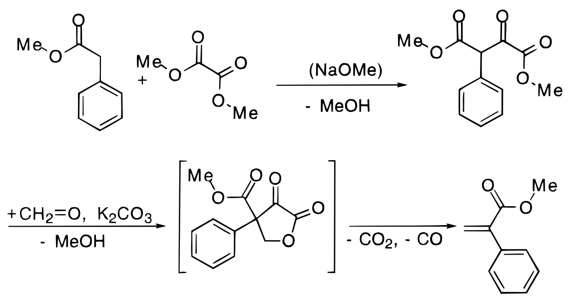
Scheme 3



2

of sodium methoxide to dimethyl 2-oxo-3-phenylsuccinate, which is converted with formaldehyde to 2-oxo-3-(methoxycarbonyl)-3-phenyl-butyrolactone. This lactone is unstable and gives **2** by cleavage of carbon dioxide and carbon monoxide. After fractional distillation **2** was obtained in 50% yield and more than 99% purity.

Copolymerization. Polymerizations were carried out at room temperature in tetrahydrofuran as solvent. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene[15] (silyl ketene acetal, **3**) was used as initiator and tetrabutylammonium bi(3-chlorobenzoate) as catalyst.[16]

Three types of reactions were made. First nearly equimolar amounts of monomers **1** and **2** were simultaneously copolymerized up to high conversion. The second type was made similarly with a 3-fold excess of monomer **1** over **2**. The third polymerization was an experiment aiming at functionalization by incorporation of one unit of **2** per chain as described by Quirk.[17] In addition a model reaction was made with an initiator/**2** ratio of nearly 1. Details of the experimental conditions of the polymerizations are given in Table 1.

Polymerizations were monitored taking samples of identical volume from the reaction mixture after different reaction times. From these samples, which had been quenched by addition of equal quantities of methanol, the conversion of monomers was determined by gas chromatography with toluene as internal standard. Aliquots of the same samples were analyzed by size exclusion chromatography using PMMA with low polydispersity as standards. Composition of copolymer from 1:1 feed was also determined by elemental analysis. Analytical properties of the different runs are summarized in Table 2.

Alternating Copolymers. Monomer consumption of run 1a as a function of reaction time is shown in Figure 1. From the very beginning of the polymerization **2** has reacted to a larger extent than **1**. The difference in consumption, however, remains constant; it is equal to the molar amount of initiator which suggests that one more unit of **2** than of **1** is incorporated in the chain.

Table 1. Experimental Conditions for the Copolymerizations of MMA (1) with Methyl α-Phenylacrylate (2)

run no.	initiator (mmol)	catalyst (mol %)	THF (mL)	monomer **1** (mmol); t (min)[a]	monomer **2** (mmol); t (min)[a]	initiator:**1**:**2**
1	1.1	1.4	30	16.2	15.4	1:14.7:14.0
1a	2.2	1.1	30	18.9	16.7	1:8.6:7.6
2	1.8	1.7	10	31.0	9.9	1:17.2:5.5
3	1.8	1.2	30	36.9 + 37.1; 160	+1.9; 100	1:41.1:1.1
4	3.9	1.4	10		4.9	1:–:1.25

[a] Reaction time before addition of monomer.

Table 2. Analytical Data of Polymer Samples

run no.	time (min)	conversion of **1** (mmol) (%)	conversion of **2** (mmol) (%)	M_n (SEC)	M_w (SEC)	M_w/M_n
1/1	25	1.9 (12)	1.3 (9)	560	680	1.22
1/2	120	5.2 (32)	4.8 (31)	1320	1530	1.16[a]
1/3	300	8.1 (50)	8.0 (52)	2000	2350	1.18[a]
1/4	600	10.0 (64)	11.1 (72)	2640	3200	1.21[a]
1/5	1340	12.0 (74)	13.0 (85)	2940	3730	1.26[a]
1/6	3000	12.5 (77)	13.5 (88)	2920	3760	1.29[a]
1a/1	20	1.7 (9)	4.7 (28)	620	680	1.09[a]
1a/2	75	4.9 (26)	9.0 (54)	1380	1500	1.09[a]
1a/3	240	9.3 (49)	11.7 (70)	2260	2630	1.16[a]
1a/4	450	11.3 (60)	13.2 (79)	2660	3220	1.21[a]
1a/5	1200	13.2 (70)	15.2 (91)	3070	3930	1.28[a]
1a/6	1740	13.2 (70)	15.0 (90)	3260	4340	1.33[a]
2/1	25	8.1 (26)	9.5 (95)	1150	1380	1.21
2/2	55	9.5 (30)	9.8 (99.5)	1190	1450	1.23
2/3	90	11.5 (37)	9.9 (100)	1290	1640	1.27
2/4	150	17.4 (56)	9.9 (100)	1550	2140	1.38
2/5	270	24.5 (79)	9.9 (100)	1880	2860	1.52
2/6	450	27.9 (90)	9.9 (100)	2030	3260	1.61
2/7	1260	28.8 (93)	9.9 (100)	2090	3390	1.62 (1.58[a])
3/1	95			2770	3210	1.16
3/2	160			2760	3230	1.17
3/3	325			2970	3470	1.17
3/4	17.5 h			4710	6520	1.38
3/5	36 h			5210	7190	1.38
4/1	10		(85)[b]			
4/2	50		(83)			
4/3	105		(88)			

[a] Neglecting the 1:1 adduct. [b] Residual **3**, 2%.

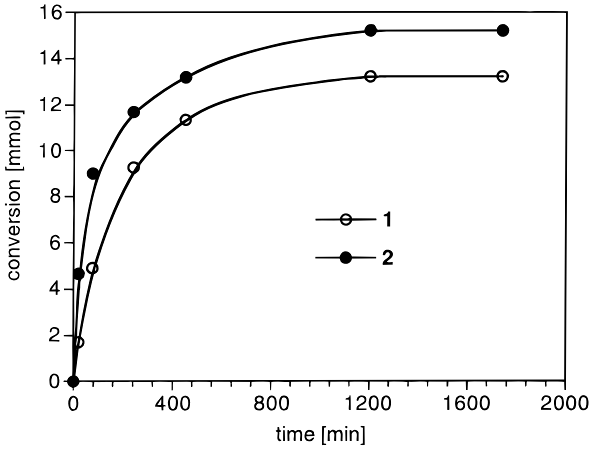


Figure 1. Monomer consumption vs. time of the copolymerization of **1** and **2** (run 1a).

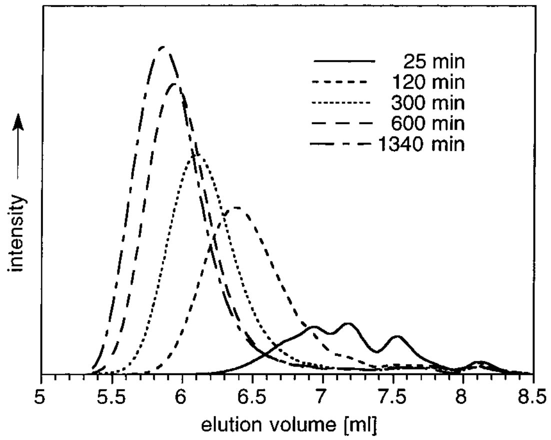


Figure 2. SEC chromatograms of copolymerization of **1** and **2** (run 1).

The size exclusion chromatograms of run 1 at different reaction times are given in Figure 2. They illustrate the increase in molecular weight and the relatively narrow molecular weight distribution. It is noteworthy that a low molar mass compound is present in the mixture even at higher conversion. This seems to be an inactive species rather than freshly formed 1:1 adduct as the initiation seems to proceed fast with respect to propagation. The polydispersity of these samples neglecting the 1:1 adduct is about 1.2. Molecular weight from SEC increases linearly with conversion as shown in Figure 3, thus supporting the living nature of the polymerization.

Conversion of monomers **1** and **2** in an experiment with a molar feed ratio of 3:1 was monitored in the same way by gas chromatography. The results are plotted in Figure 4. In the first period of the reaction (30−40 min) consumption of both monomers is similar to the previous experiment; i.e., an alternating copolymer is formed. When **2** is almost completely incorporated, the rate of conversion of **1** slowly increases and then decreases with the concentration of **1** in the feed. This suggests formation of a block copolymer consisting of a poly(**1**, **2**) and a poly(**1**) block (cf. Scheme 4). Samples taken before total consumption of **2** have a polydispersity comparable to the alternating copolymers from run 1 (Table 2). Block formation, however, results in a broadening of the molecular weight distribution to 1.6.

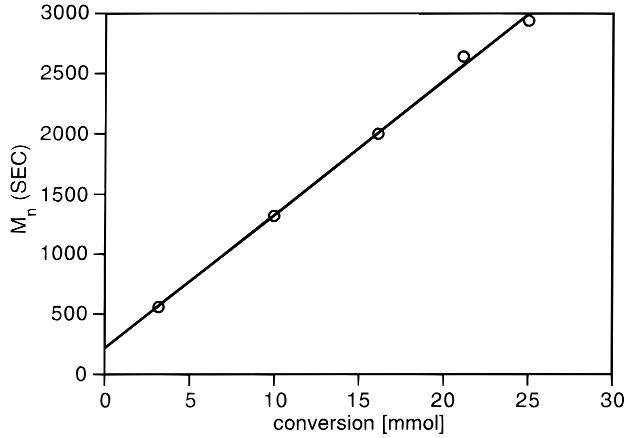


Figure 3. Molecular weight vs. conversion of copolymerization of **1** and **2** (run 1).

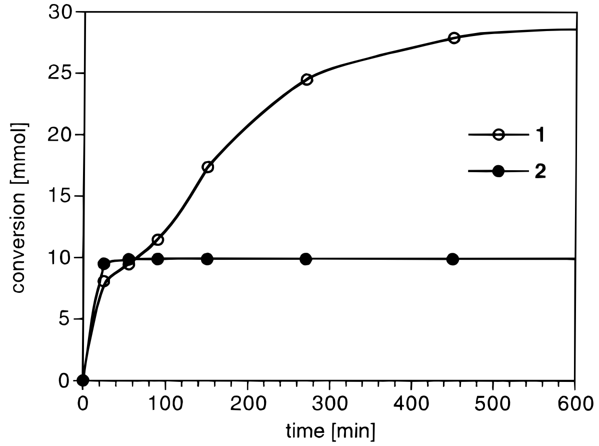
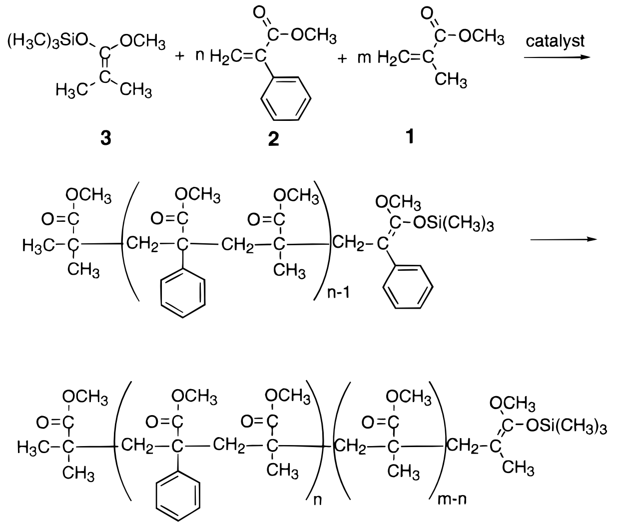


Figure 4. Conversion of monomers in the copolymerization of **1** and **2** with a molar feed ratio of 3:1 (run 2).

Scheme 4



Further insight into the nature of this polymerization is gained by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF−MS). Two samples of run 1 with equimolar amounts of monomers in the feed 1/1 and 1/3 and two samples of run 2, namely 2/1 and 2/7, were investigated this way. The spectra are shown in Figures 5−8. With LiCl as ionizing aid the molar mass of a molecule is increased by 6.94. The structures and mass increments of the initiator fragment, of the two monomers and of the

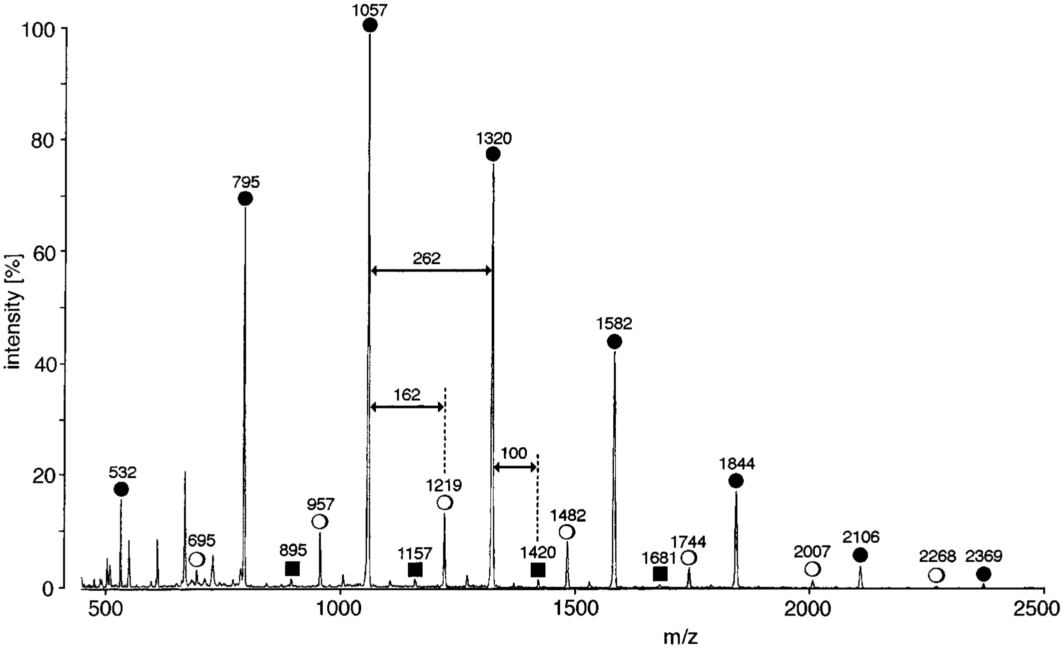


Figure 5. MALDI–TOF mass spectrum of 1/1 (100% intensity = 427 mV).

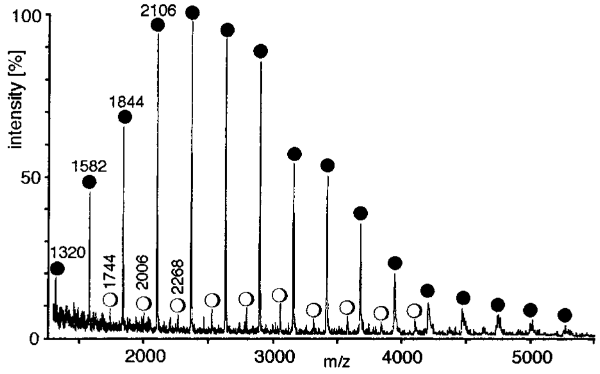


Figure 6. MALDI–TOF mass spectrum of 1/3 (100% intensity = 18 mV).

alternating diad are given in Scheme 5. Thus MMA (**1**) has an increment of 100.12, **2** an increment of 162.19, and an alternating diad an increment of 262.31 (due to the resolution of the mass spectrometer only integer numbers are used in the discussion).

In Figure 5 three homologous series with mass increments of 262 can be seen, which proves that an alternating copolymer is formed. The molecular weight of the series with highest intensity can be described by $101 + (262)_n + 162 + H + Li$, where 101 is the mass of the initiator fragment. The molecular weight of the homologues of the second series is by 100 mass units lower or, which is equivalent, 162 mass units higher $[101 + (262)_n + (162)_2 + H + Li]$. The third series with very low intensity contains one MMA unit more or one unit of **2** less in the molecule than the main product $[101 + (262)_n + H + Li]$. In terms of composition this means: **2** obviously is added as first monomer to the active site of the initiating system and then alternating copolymerization proceeds with **2** also as last monomer unit for the series with highest intensity. The second series has one unit of **2** more incorporated than required for an alternating copolymer. If this "error" occurred statistically further series with a shift of $n \times 162$ were to be expected. The third series can have its origin from MMA as first incorporated unit, as terminal unit or from non alternating sequences (multiple incorporation of **1**).

This picture is not changed with higher conversion (Figure 6). The intensity of the second series decreases with respect to Figure 5; other homologous series cannot be distinguished from the noise because the peak intensity decreases for higher molecular weight samples.

The excess of MMA in run 2 has only a minor influence on the composition of the copolymer as long as monomer **2** is still present in reasonable amounts. This is shown in Figure 7 for sample 2/1. Again only alternating copolymers are formed but four homologous series can be distinguished this time. The series with **2** as the first and the last unit incorporated has the highest intensity, while the intensities of the two other series also present in run 1 have changed. The series $101 + (262)_n + H + Li$ with one additional MMA incorporated has higher intensity than the series $101 + (262)_n + (162)_2 + H + Li$ with **2** in excess. The new homologous series $101 + (262)_n + 100 + H + Li$ has two MMA more than the main series. This demonstrates that multiple addition of **1** can occur at least in the final stage of the alternating copolymerization when the concentration of **2** becomes very small while less than one-third of MMA has reacted if the monomer feed ratio is 3:1.

The MALDI–TOF mass spectrum after almost complete conversion of both monomers shown in Figure 8 has a great multitude of peaks with very low intensity. Mass increments of 100 prevail, but the original alternating copolymer is present to a considerable extent. This can be due either to an easier ionization of the alternating structure with respect to the block copolymer or to the fact that some deactivation of living chains has occurred during removal of samples from the reaction mixture. The noiselike shape in Figure 8 is what one should expect because each of the living homologues of the alternating polymer should start a new homologous series with increments of 100 (MMA). Some of these have been marked in Figure 8.

End-Functionalized PMMA. The results obtained with the alternating copolymerization and block copolymerization experiments of **1** and **2** prompted us to

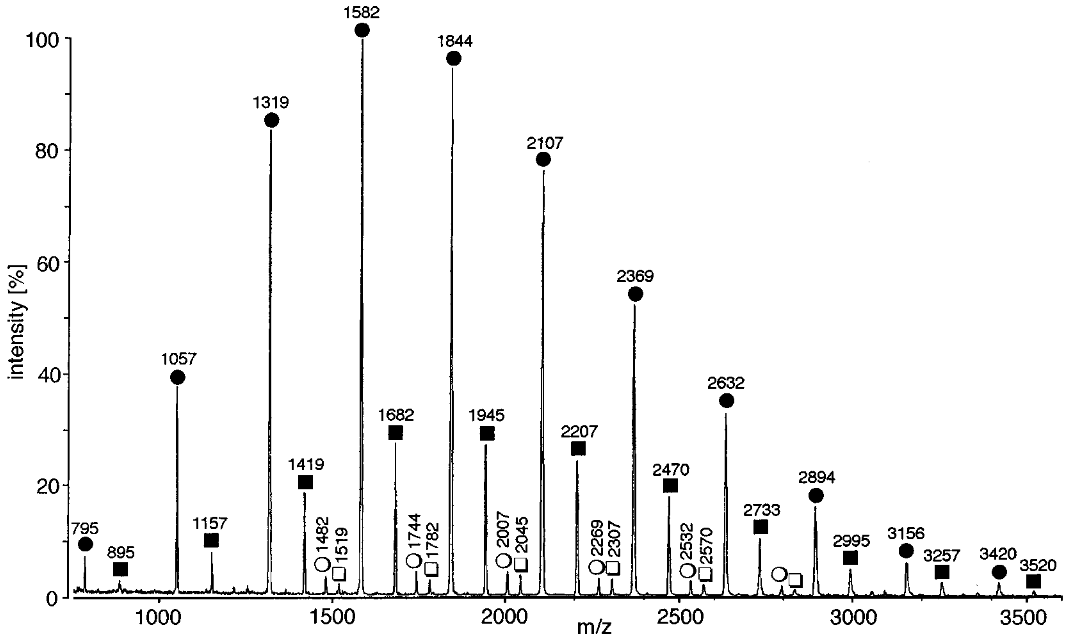


Figure 7. MALDI−TOF mass spectrum of 2/1 (100% intensity = 287 mV).

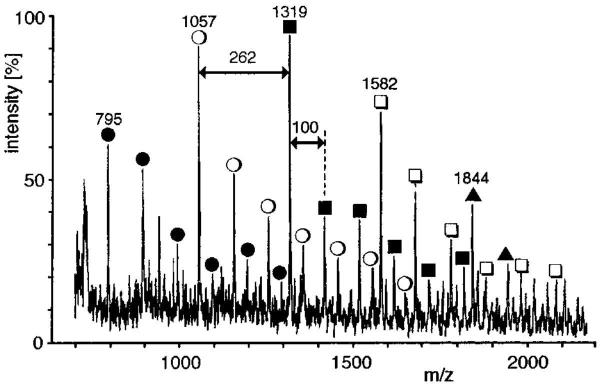
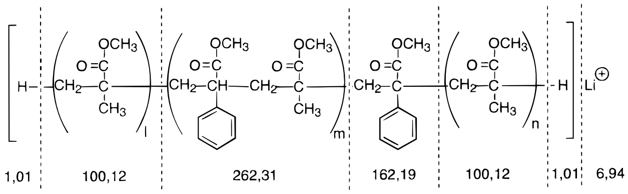


Figure 8. MALDI−TOF mass spectrum of 2/7 (100% intensity = 11 mV).

Scheme 5. Structure and Mass Increments of Polymers 1−3



1: l = 1, m, n = 0; 2: l = 1, m, n; 3: l, m = 0-2, n

have a closer look at the experiments on living functionalization of PMMA with **2** reported by Quirk and co-workers.[17] Living PMMA was synthesized (Table 1, entry 3) and reacted with a slight excess of **2** with respect to the living chains. Samples were taken in the usual way before and after the addition of **2** to ensure complete conversion of **1** and complete functionalization with **2**. MMA was added to the functionalized polymer, and the polymerization was monitored by SEC of samples which were taken at different times after the second addition of MMA.

The MALDI−TOF mass spectrum of the sample taken after functionalization is shown in Figure 9. There is only one homologous series with a molar mass 101 + $(100)_n$ + 162 + H + Li confirming the addition of just one molecule of **2** per living chain. Addition of further MMA to the reaction mixture leads to incorporation of excess **2** after reaction of MMA with the **2**-terminal of the chain. This causes formation of two further homologous series 101 + $(100)_n$ + $(162)_2$ + H + Li and 101 + $(100)_n$ + $(162)_3$ + H + Li, which are distinguished from the main one by the incorporation of two and three units of **2** per living chain as is shown in Figure 10.

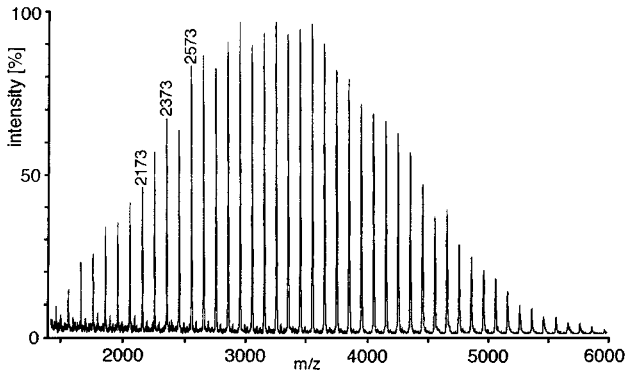


Figure 9. MALDI−TOF mass spectrum of 3/2 (100% intensity = 42 mV).

An experiment directed to investigate the homopolymerization behavior of **2** was made by reaction of **3** and **2** in a feed ratio of 1:1.25. The reaction was monitored by gas chromatography. After 10 min, more than 95% of the silyl ketene acetal **3** and 85% of **2** had reacted, if the sample had not been deactivated with methanol. A deactivated sample had higher conversion of **2**, which suggests multiple addition of **2** to some extent. The 1:1 addition product dimethyl 2-phenyl-4,4-dimethylglutarate was isolated from this mixture by distillation in 89% yield. MALDI−TOF−MS investigation of the deactivated sample gave a peak for the single and for the double addition product. The intensities, however, do not reflect the true ratio because the 1:1 adduct is volatile in the vacuum of the spectrometer. If the difference in the yield of the 1:1 adduct to 100% is attributed to the formation of a 1:2 addition product, approximately 10% of double addition has taken place.

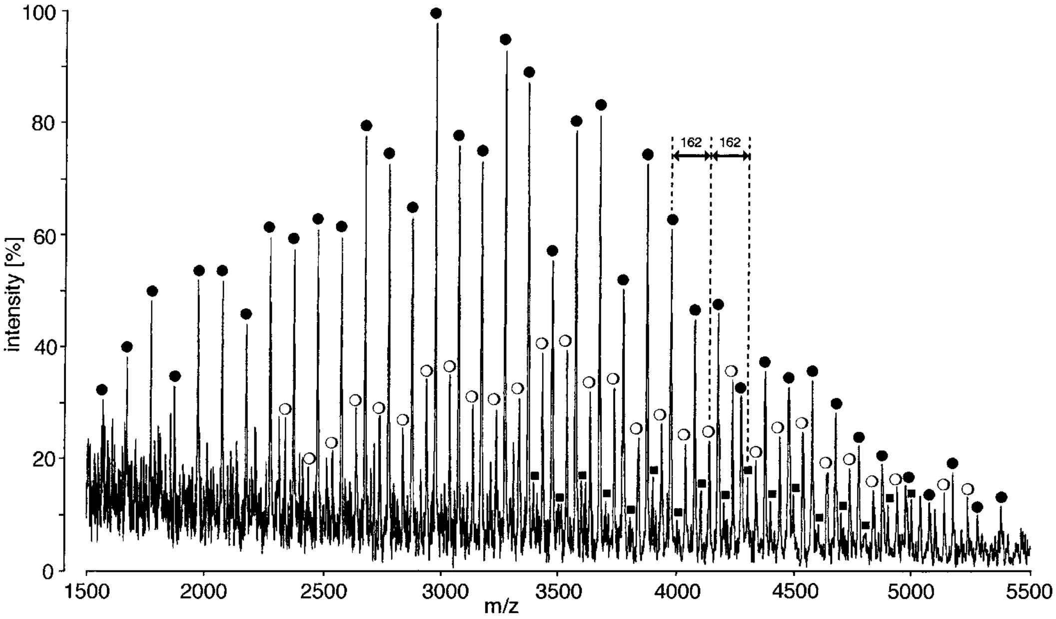


Figure 10. MALDI−TOF mass spectrum of 3/3 (100% intensity = 8 mV).

These results can explain the homologous series with one unit of **2** more than required for a strictly alternating copolymer having **2** as first and last monomer unit as observed in the MALDI−TOF mass spectra of the alternating copolymers (Figures 5 and 7).

Discussion

The results presented in the previous section give the following picture. Methyl α-phenylacrylate **(2)** gives exclusively single addition to the living center in a group transfer polymerization at room temperature. This is due to the ceiling temperature of **2**, a fact which has been used for the living functionalization of PMMA with **2**.[17] The influence of the ceiling temperature could also be demonstrated from the difference in conversion found between deactivated and living oligomers in gas chromatography. Double addition of **2** seems to be possible to some extent in the first two steps of the reaction of the active center as shown in the model reaction of **2** under GTP conditions. This is most likely the reason for the homologous series with one additional **2** incorporated than required for an alternating copolymer with **2** as the first and the last monomer unit.

Rate constants for the different propagation steps have not been determined. The conversion/time diagrams in Figures 1 and 4 together with MALDI−MS results suggest the following order of rate constants. Addition of **2** to an MMA-terminal (k_{12}) is faster than addition of **1** to a **2**-terminal (k_{21}). The turning point in the MMA conversion curve in Figure 4 proves that the rate of conversion of **1** increases when homopolymerization is the predominant or exclusive reaction. Therefore k_{11} is bigger than k_{21}. Finally, as no homopolymerization of **2** is possible at room temperature, k_{22} is zero. According to the copolymer equation formation of alternating copolymers requires that cross propagation is highly favored over homo propagation; i.e., $k_{12} >> k_{11}$ and $k_{21} >> k_{22}$, a condition which certainly is fulfilled in this case. On the basis of the information gained from the experiments the order of rate constants for the different propagation reactions is $k_{12} >> k_{11} > k_{21} >> k_{22}$.

Living functionalization of living GTP-PMMA with methyl α-phenylacrylate gives complete and selective monoaddition even in the presence of excess **2**, thus proving the results reported by Quirk.[17] As we could show excess **2** is incorporated when MMA is present in the reaction mixture. It should be possible to synthesize a polymer by GTP which is essentially a PMMA having marks or labels of one methyl α-phenylacrylate in a regular fashion.

Polydispersity of the alternating copolymers is in the range known from homo group transfer polymerization. One would expect some broadening if block copolymers are made because of $k_{11} > k_{21}$, which should have a similar effect as a slow start reaction in relation to propagation. The relatively high polydispersity in run 2 is most likely due to some termination occurring during each removal of a sample from the reaction mixture.

Conclusions

Methyl methacrylate and methyl α-phenylacrylate were copolymerized by GTP and the copolymers investigated by MALDI−TOF mass spectrometry. This method is a powerful tool to learn about the microstructure of the polymers. The high tendency to form alternating copolymers can be explained by the ceiling temperature of poly(**2**), which allows addition of only one monomer to the active chain and by the higher rate of addition of **2** to the living MMA terminal as compared to the addition of **1** (homo propagation).

Experimental Part

Materials. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (initiator) and tetrabutylammonium bi(3-chlorobenzoate) (catalyst) were prepared according to procedures described in the literature.[15,16] Methyl methacrylate (MMA) was stirred over CaH_2, distilled under reduced pressure and stored at −20 °C under argon atmosphere up to 48 h prior to use. THF was distilled from potassium into the reaction flask immediately prior to use. Toluene as internal standard for gas chromatography was distilled from sodium.

Methods of Characterization. Infrared spectra: Bruker IFS48-FTIR spectrometer as films between NaCl plates. NMR spectra: Bruker AC-200 (200 MHz for ^{1}H-spectra, 50 MHz for ^{13}C-spectra) using deuterochloroform with TMS as internal standard. Size exclusion chromatography (SEC): Thermo Separation Products P100 pump, Shodex RI-71 refractive index detector, Polymer Standards Service 100 Å SDV-gel column, THF as eluent, PMMA standards from Polymer Standards Service for calibration. MALDI−TOF−MS: Kratos Kompakt MALDI 3; matrix, 2,5-dihydroxybenzoic acid; solvent, THF; ionization promotor, LiCl; calibration standard, PEG 4000. Conditions: 20 kV acceleration voltage, 150 shots per sample, polarity, positive; flight path, reflection. Elemental analyses: Mikroanalytisches Labor Beller, Göttingen, Germany.

Methyl α-Phenylacrylate (2).[14] In a 500 mL flask, 0.5 mol of sodium methoxide was prepared by addition of methanol to 0.5 mol of finely divided sodium in 200 mL of toluene. To this suspension a mixture of 59 g (0.5 mol) of dimethyl oxalate and 100 g (0.67 mol) of methyl phenylacetate was added slowly through a dropping funnel. After the mixture was stirred overnight, the yellow sodium salt was collected, washed with toluene and ether, and acidified with hydrochloric acid. The aqueous solution was extracted with ether, and dimethyl 2-oxo-3-phenylsuccinate was isolated by evaporation of volatiles. The crude oxalo ester was mixed with 60 mL of 37% aqueous formaldehyde solution and 50 mL of water, 54 g potassium carbonate in 100 mL of water was slowly added, and the mixture was stirred for 2 h. Layers were separated, the aqueous layer was extracted with ether, and the combined organic layers were dried with sodium sulfate. After evaporation of the ether, the residue was distilled in vacuo (106−108 °C / 11 mbar) to give 40 g (0.25 mol) methyl α-phenylacrylate (50%, Lit.:[14] 88%). For further purification the ester was converted to the acid, which was recrystallized and again esterified. The purity was greater than 99% (GC). ^{1}H-NMR: δ = 7.2−7.6 (m, 5H), 6.37 (s, 1H), 5.89 (s, 1H), 3.82 ppm (s, 3H). ^{13}C-NMR: δ = 167.2 (C═O), 141.2, 136.6, 128.2, 128.1, 128.0, 126.8 ($\mathrm{C_{olefin}}$, $\mathrm{C_{arom}}$), 52.1 ppm (C—O). IR: 3056, 3024 ($\mathrm{C{-}H_{olefin}}$), 2952 ($\mathrm{C{-}H_{aliphat}}$), 1722 (C═O), 1616 cm^{-1} (C═C).

GTP of Methyl Methacrylate and Methyl α-Phenylacrylate. A flame-dried 100 mL (50 mL for run 4) three-necked round-bottomed flask equipped with argon inlet, magnetic stirring bar, thermometer, and rubber septum was charged with the amounts of THF, initiator and catalyst given in Table 1. Monomers or mixtures of monomers (cf. Table 1) were added dropwise to the stirred solution through the septum with a syringe at a rate of 1 mL/min. A temperature increase indicated that polymerization took place. After reaction times given in Table 2, samples of 2 mL (1 mL for runs 2 and 4) were taken with a syringe and quenched immediately with 0.2 mL of methanol (0.1 mL for runs 2 and 4). Conversion of monomers was determined by gas chromatography with toluene as internal standard. Molecular weight distribution over time was followed by SEC (see Table 2). When there was no further reaction, the mixture was quenched with methanol. Polymers were precipitated in heptane, freeze-dried from $\mathrm{CCl_4}$ and dried at 80 °C in vacuo. Anal. Alternating copolymer from run 1a: C, 68.67 (calcd: 68.64), H, 6.97 (calcd: 6.94).

Functionalization of PMMA (Table 1, Entry 3). One hour after the temperature maximum an aliquot of the reaction mixture was withdrawn by syringe and quenched with methanol. Then the amount of methyl α-phenylacrylate **(2)** given in Table 1 was added to the reaction mixture through the septum with a syringe. A second sample was taken before the addition of a second amount of MMA. After reaction of MMA the living polymers were quenched with methanol.

Dimethyl 2-Phenyl-4,4-dimethylglutarate. After 105 min the reaction (run 4, Table 1) was stopped by addition of methanol, volatiles were removed in vacuo at room temperature, and the residue was distilled in a Kugelrohr apparatus (100−140°C / 0.04 mbar). Yield: 89%. ^{1}H-NMR: δ = 7.1−7.4 (m, 5H), 3.62 (s, 3H), 3.6−3.7 (m, 1H), 3.50 (s, 3H), 2.47 (dd, 1H), 2.04 (dd, 1H), 1.19 (s, 3H), 1.18 ppm (s, 3H). ^{13}C-NMR: δ = 177.3, 174.4 (C═O), 139.5, 128.6, 127.8, 127.2 ($\mathrm{C_{arom}}$), 52.0, 51.6, (C—O), 48.1, 43.7, 41.9 ($\mathrm{CH_2}$, CH, $\mathrm{CR_4}$), 26.1, 24.5 ppm ($\mathrm{CH_3}$). IR: 2952 (C—H), 1734 ($\mathrm{C{=}O_{ester}}$), 1600 cm^{-1} ($\mathrm{C{=}C_{arom}}$).

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