Preparation of α-Phenyl Ketone-, ω-Carboxylate-Ended Telechelic Methyl Methacrylate Oligomers by the Ozonolysis of Regioregular Methyl Methacrylate–Phenylacetylene Copolymers

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ABSTRACT: Telechelic methyl methacrylate oligomers with α-phenyl ketone and ω-carboxylic acid end groups have been prepared by the ozonolysis of statistical copolymers of methyl methacrylate and phenylacetylene. The oligomers are exclusively α-phenyl ketone- and ω-carboxylate-ended, indicating that the incorporation of phenylacetylene in the parent copolymer is regiospecific. The oligomers have number-average molecular weights ranging from 1600 to 4500 (controlled by the composition of the copolymers from which they were prepared) and polydispersities of less than 2.

Introduction

In order to be able to produce high molecular weight specialty polymers that are not accessible by conventional chain-reaction and step-reaction homo- and copolymerizations, access to a wide range of short polymer blocks with terminal reactive end groups (telechelic oligomers) is desirable. Telechelic oligomers are useful precursors as they can be chemically extended in a variety of ways and in a variety of combinations to produce novel block and graft copolymers.

Telechelic oligomers conventionally are prepared by a number of techniques, including by anionic polymerization, group transfer polymerization, and radical and cationic polymerization, using functionalized initiators and transfer or terminating agents. An attractive alternative involves the controlled scission of a high molecular weight copolymer containing a small amount of a readily cleavable "weak-link" comonomer unit, e.g., oxidative cleavage of an unsaturated unit derived from a diene, a procedure first exploited in a significant way by Maillard *et al.*,[1] Jones and Marvel,[2] and Guizarde and Cheradame[3] for the production of telechelic hydrocarbon oligomers. The advantages of the approach (which we have recently dubbed "constructive degradation") are that the distribution of oligomer chain lengths follows the most probable distribution ($M_w/M_n \leq 2$) and is therefore relatively narrow, that access is gained to a wide range of oligomer types not easily made by the more conventional routes (e.g., oligomers based on functional and water-soluble monomers), that end-group functionalities are generally high (better than 98% if each chain of the starting polymer is cleaved at least 100 times), and that good control can be exercised over the types of end groups (controlled by the scission chemistry and the method of workup of the scission products).

Using the constructive degradation approach, we have produced recently a range of telechelic acrylic oligomers with carboxylic acid, hydroxyl, or ketone end groups by ozonolyzing the in-chain double bonds of acrylic co- and terpolymers prepared by radical copolymerizations of acrylics with selected 1,3-dienes.[4,5] However, the use of 1,3-dienes to introduce in-chain unsaturation suffers from the disadvantage that some pendent unsaturation in the form of 1,2-diene units may be introduced also, leading to unwanted additional functionality in the final oligomers. This problem can potentially be avoided by use of an acetylenic monomer to introduce the unsaturation rather than a diene. In this paper, we report the preparation, by low conversion radical copolymerization, of high molecular weight copolymers of methyl methacrylate (MMA) and phenylacetylene (PA) containing 4, 8, 10, and 13 mol % PA units and the subsequent ozonolysis of them to give exclusively α-phenyl ketone-, ω-carboxylate-ended telechelic MMA oligomers. The work has already been communicated in a preliminary form elsewhere.[6]

Results and Discussion

Copolymer Compositions, Microstructures, and Molecular Weights. The 60-MHz ^{1}H NMR spectrum of MMA/PA copolymer **3** is shown in Figure 1; it contains phenyl (H_A) and olefinic methine (H_B) signals arising from PA units (7.1–7.6 and 5.5–5.8 ppm, respectively) and methoxyl (H_C), β-methylene (H_D), and α-methyl (H_E) signals from MMA units (0.8–1.7, 1.7–3.1, and 3.2–4.1 ppm, respectively). The small components of the methoxyl resonances at 3.4 and 3.5 ppm are believed to arise from MMA units adjacent to PA units in the copolymer chains. These components increase in size relative to the main methoxyl peak as the PA content of the copolymer increases. Similar upfield shifts of MMA methoxyl signals are seen in the ^{1}H NMR spectra of MMA/styrene copolymers.[7] The mole fractions of MMA in the MMA/PA copolymers have been determined by comparison of the areas of the PA phenyl proton signals with the total proton signal areas in the ^{1}H NMR spectra and are given in Table 1. Alternatively, the compositions may be determined by comparison of the PA phenyl signals with the MMA methoxyl signals, but as these latter signals are not completely resolved from a minor component of the MMA β-methylene resonances centered at 3.0 ppm, the former method is considered to be more reliable. The average molecular weights of the copolymers determined by GPC also are given in Table 1. As can be seen from the table, all the copolymers have number-average molecular weights (M_n) in the range (90–170) × 10^3 (polystyrene equivalents). It is important that the molecular weights of the starting copolymers are high if the oligomers produced from them by chain scission are to have end groups derived mainly from the scission process and only very low concentrations of end groups corresponding to those of the original copolymer.

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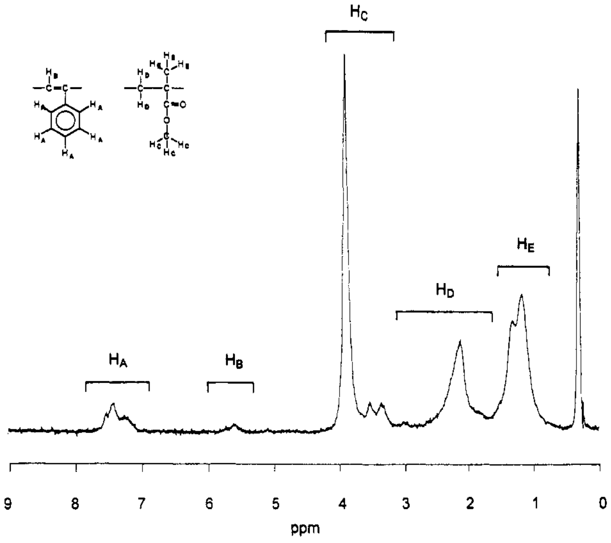


Figure 1. 60-MHz ^{1}H NMR spectrum of MMA/PA copolymer 3.

Table 1. Mol Fractions of MMA in the Monomer Feeds and in the Resulting MMA/PA Copolymers Measured by ^{1}H NMR

copolymer	mol fraction of MMA in feed	mol fraction of MMA in copolymer	M_n	M_w	M_w/M_n
1	0.96	0.96	170 750	407 520	2.38
2	0.92	0.92	148 670	342 170	2.30
3	0.89	0.90	113 640	256 600	2.26
4	0.85	0.87	90 520	198 520	2.19

Initial estimates of the reactivity ratios for the copolymerization of MMA and PA have been calculated from the composition data given in Table 1 using the Kelen–Tudos procedure;[8] these estimates are found to be $r_{MMA} = 0.93$ and $r_{PA} \approx 0$, indicating that the polymers will contain mainly isolated PA units. Assuming that r_{PA} is indeed equal to zero (PA certainly shows no propensity to homopolymerize with radical initiators), the optimum value of r_{MMA} has then been found by an iterative process in which r_{MMA} is varied systematically until the sum of the squares of the deviations of the calculated copolymer compositions (based on the reactivity ratios) from the measured compositions is minimized. The optimum value of r_{MMA} found in this way, and used later to estimate mean MMA sequence lengths in the copolymers, is 0.97. A better estimate of r_{MMA} could be found, in theory at least, using the recently published method of Bauduin and Boutevin.[9] However, application of this method would require the carrying out of copolymerizations to maximum conversion and the determination of residual, unconsumed MMA, a procedure also likely to be subject to considerable error. The ^{1}H NMR spectra and the reactivity ratio data are thus consistent with the copolymers having the structure 1 shown in Scheme 1.

Structures of the Oligomers. Consideration of the chemistry of formation of the oligomers (Scheme 1) indicates that they are expected to have, on average, one carboxylic acid end group and one phenyl ketone end group per chain.

The ^{1}H NMR and ^{13}C NMR spectra of all the oligomers are similar; those for oligomer 3 are shown in Figures 2 and 3, by way of example. The spectra indicate that most if not all of the double bonds in the parent copolymers are cleaved; in the ^{13}C NMR spectrum there are no olefinic carbon signals between 125 and 140 ppm, and in the ^{1}H NMR spectrum there are no olefinic methine and methylene proton signals between 4.5 and 5.6 ppm. In the ^{1}H NMR spectrum, aromatic proton signals at 7.2–7.8 ppm (H_A in Figure 2) are consistent with those expected for oligomers with terminal phenyl ketone end groups, as are the aromatic carbon signals at 127–137 ppm in the carbon spectrum (C_A in Figure 3). Of particular interest is the peak at 197 ppm in the ^{13}C NMR spectrum which is characteristic of the carbonyl carbon in a phenyl ketone end group (C_B). As expected, the intensity of this phenyl ketone end-group peak relative to those from the repeat units increases with decreasing M_n of the oligomers. The carbonyl carbon signal from the carboxylic acid end group is probably obscured by the ester carbonyl carbon signals of the methyl methacrylate units at 175–178 ppm.

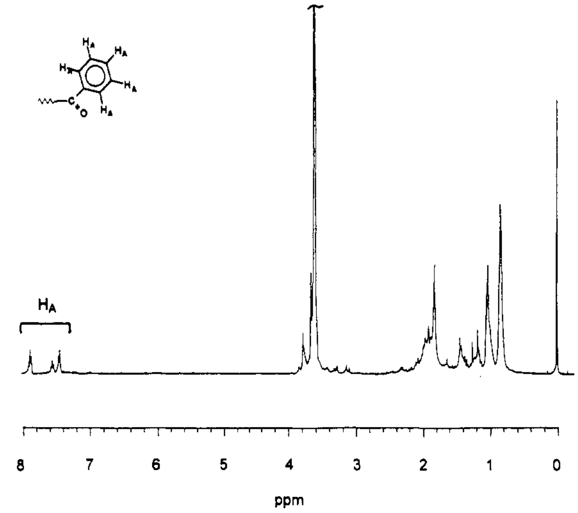


Figure 2. 400-MHz ^{1}H NMR spectrum of oligomer 3 (derived from copolymer 3).

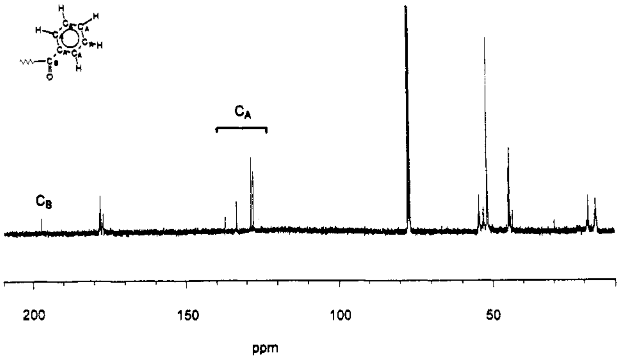
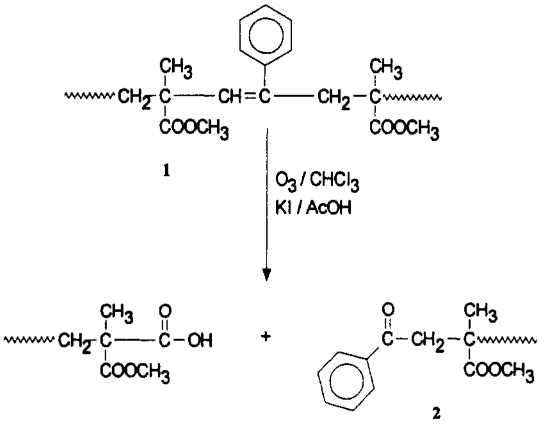


Figure 3. 100-MHz ^{13}C NMR spectrum of oligomer 3.

Scheme 1



That only one phenyl ketone carbonyl resonance is visible in the ^{13}C NMR spectra of the oligomers, indicates that the phenylacetylene units have been incorporated in the parent copolymers in a regiospecific manner. We

Chart 1

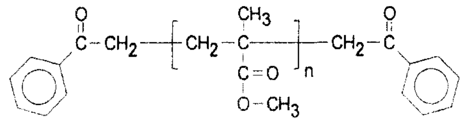


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Chart 2

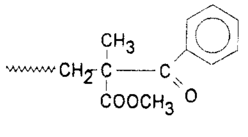

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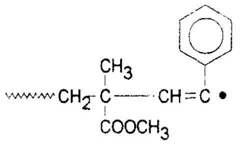
Chart 3



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believe that the phenyl ketone end group has uniquely the structure **2** shown in Scheme 1. This structure is identical to that of one of the end groups found in MMA oligomers prepared by ozonolysis of MMA/2,3-diphenylbuta-1,3-diene copolymers, which show two phenyl ketone carbonyl resonances (at 199 and 197 ppm, respectively[4]) arising from the end-group carbonyls in structure **3** (Chart 1).

Assignment of the chemical shifts of the ketone carbonyl carbons in **3** is difficult as only the β and γ substituents are different. However, it has been shown that ketone carbonyl carbons are progressively deshielded as the substitution of the α carbon is increased.[10] As a consequence the structure of the end groups in the telechelics prepared from MMA/PA copolymers is more likely to be as shown in **2**, since the alternative end-group structure (**4** in Chart 2) would contain a ketone carbonyl with a quaternary α-carbon, and consequently to be predicted to have a chemical shift greater than that of either of the ketone carbonyls in **3**. The incorporation of PA into the parent copolymer must, therefore, have been *via* the more stable PA radical, **5** (Chart 3), as expected.

Molecular Weights of the Oligomers. As ozonolysis proceeded, a noticeable drop in viscosity of the copolymer solution was observed. The final oligomers are viscous liquids at room temperature but become glassy below −10 °C. The oligomers are freely soluble in many organic solvents but are only moderately soluble in methanol. The molecular weights and polydispersities of these oligomers have been determined by GPC and by end-group analysis (titration of carboxylic acid end groups and ^{1}H NMR analysis for phenyl ketone end groups) and are given in Table 2. The GPC trace of oligomer **3** is shown in Figure 4; partial resolution of individual oligomers can be seen on the low molecular weight side of this trace at elution times between 27 and 32 min.

Table 2 also contains theoretical values of M_n and M_w/M_n calculated from the optimized reactivity ratios. The calculations make use of the well-known statistical relationships[11] $P_n = 1/P_{12}$ and $P_w = (2 - P_{12})/P_{12}$, where P_n and P_w represent respectively the number-average and weight-average lengths of M_1 sequences (here sequences of MMA units) and P_{12} represents the probability of adding an M_2 unit to a growing chain ending in an M_1 unit. P_{12} is given by $P_{12} = 1/(r_1F_1/F_2 + 1)$, where F_1 and F_2 are the mole fractions of M_1 and M_2 in the feed. The theoretical P_n and P_w values are used, in turn, to calculate theoretical M_n and M_w values for the oligomers assuming that all M_2 (PA) units are cleaved and that all the end groups of the resulting MMA oligomers are phenyl ketone and carboxylic acid (in equal amounts). The relevant relationships are $M_n = P_n \times 100 + 150$ and $M_w = P_w \times 100 + 150$ (*n.b.* 100 is the molar mass of the MMA repeat unit and 150 is the sum of the masses of one phenyl ketone and one carboxylic acid end group).

The M_n values of the oligomers determined by titrimetric analysis and by ^{1}H NMR (calculated assuming one carboxylic acid end group and one phenyl ketone end group, on average, per chain), although not in good agreement, are similar but are consistently slightly larger than those obtained by GPC. The discrepancies between the various estimates of M_n are probably merely a reflection of various forms of experimental error. In particular it is likely that titrimetric analysis will tend to underestimate M_n since the neutralization of the acid groups on the chain is rather slow and the natural tendency is to overshoot the end point. Also, in GPC it is likely that the carboxylic acid end groups of the oligomers will interact with the column packing, leading to delayed elution and hence to artificially low molecular weights being obtained by this technique. That the measured M_n values are all higher than those calculated we take to indicate slight error in the measured reactivity ratios, although incomplete ozonolysis cannot be entirely excluded, despite the apparent absence of signals from olefinic groups in the NMR spectra of the oligomers, given the relatively low sensitivity of the NMR technique. The polydispersities determined by GPC are, with the exception of that for oligomer 1 (the oligomer of highest average molecular weight), lower than those calculated from reactivity ratios and copolymer compositions. We attribute this to slight loss of the lowest molecular weight (most volatile) fraction during removal of solvent from the oligomers by rotary evaporation. This effect has been seen also in some of our previous studies.[4,5]

Conclusions

The constructive degradation of MMA/PA copolymers using ozone produces oligomers with exclusively α-phenyl ketone and ω-carboxylate end groups. The phenyl ketone end groups of the oligomers (and by implication also the carboxylic acid end groups) appear, from ^{13}C NMR evidence, to be all of one type, indicating that the original copolymers from which the oligomers are made are perfectly regioregular. The molecular weights of the telechelic oligomers can be controlled by altering the compositions of the parent copolymers. A small degree of fractionation of the oligomers occurs during workup, leading to slightly lower polydispersities than are predicted. The telechelic oligomers have applications in the synthesis of novel block and graft copolymers, and we shall be reporting on some of these in due course.

Experimental Section

Purification of Monomers. MMA (Aldrich) was freed from hydroquinone inhibitor by washing (three times) with a 10% aqueous NaOH solution followed by distilled water and then dried over anhydrous Na_2SO_4. PA (Aldrich) exhibited no sign of impurity when examined by ^{1}H NMR in a $CDCl_3$ solution and was therefore used as supplied.

Preparation of Statistical Copolymers. Statistical copolymers of MMA with PA were prepared by low-conversion free-radical polymerizations of mixtures of the two monomers under vacuum at 60 °C in Pyrex glass ampules (20–200 mL), using toluene as solvent. All copolymerizations were carried out

Table 2. Molecular Weights and Polydispersities of the Oligomers

parent copolymer	derived oligomer	M_n NMR[a]	M_n chem[b]	M_n GPC[c]	M_w/M_n (GPC)[c]	M_n (calc)[d]	M_w/M_n (calc)[d]
1	1	4460 ± 100	3650 ± 80	2560 ± 130	1.96	2578	1.86
2	2	3340 ± 100	2820 ± 70	2010 ± 110	1.67	1366	1.82
3	3	2190 ± 100	1970 ± 40	1500 ± 90	1.47	1035	1.76
4	4	1610 ± 100	1290 ± 30	1000 ± 60	1.58	800	1.69

[a] Determined by comparison of the end-group phenyl and main-chain methoxyl proton signals. [b] Determined by titration of the carboxylic acid end groups with methanolic KOH. [c] GPC analysis in THF with a polystyrene calibration. [d] Calculated from feed compositions and optimized reactivity ratios (see text for details).

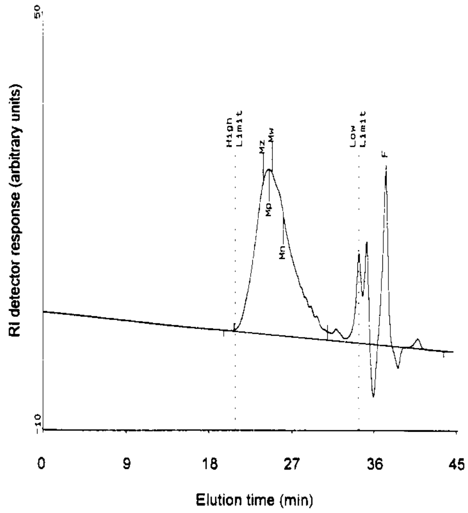

Figure 4. GPC trace of oligomer **3** in a THF solution.

at an overall monomer concentration of 5 mol L^{-1} with benzoyl peroxide (1 g L^{-1}) as initiator. The polymerizations were quenched at 5–10% conversion by rapid cooling, and the copolymers were recovered by precipitation in 5 times the reaction volume of vigorously stirred methanol and then dried to constant weight under vacuum at room temperature. The copolymers were stored in the dark at approximately 0 °C prior to use. Number-average (M_n) and weight-average (M_w) molecular weights of the copolymers were measured by gel permeation chromatography (GPC) in THF using a Waters 510 chromatograph equipped with a Waters refractive index detector and two 60-cm Polymer Laboratories columns packed with 10-μm PLgel beads of mixed porosity. The columns were calibrated using narrow molecular weight polystyrene standards.

Preparation of the Telechelic Oligomers. Samples of the copolymers (1–15 g) were dissolved in dry chloroform (8% w/v), and ozone, in a stream of dry oxygen, was bubbled through the solutions at 0 °C for up to 8 h. The electric discharge ozone generator (Wallace and Teirnan) delivered 1.74 g O_3 h^{-1} at a total flow rate (O_2 + O_3) of 45 L h^{-1}, as determined by titration of iodine liberated from a standard KI solution. The ozonides were decomposed using KI in acetic acid at 0 °C.[12] The oligomers were recovered by washing the chloroform solution with water until the washings were neutral, removing the iodine by washing with 5% w/v aqueous sodium thiosulfate, and then drying over anhydrous Na_2SO_4. The chloroform was removed by rotary evaporation at room temperature to give MMA oligomers with yields of >95 mol %. M_n and M_w of the oligomers were measured by GPC in THF using a Waters 510 chromatograph equipped with two 60-cm Polymer Laboratories columns packed with 5-μm PLgel beads of 500 and 100 Å, respectively. M_n values were determined also by titration of the carboxylic acid end groups in 0.5-g samples of oligomers dissolved in $CHCl_3$ with standardized methanolic KOH, using phenolphthalein as indicator, and by NMR end group analysis.

NMR Measurements. ^{1}H NMR (60 and 400 MHz) and ^{13}C NMR (100 MHz) spectra of the copolymers and the oligomers were recorded on 15% w/v solutions in $CDCl_3$ (99.8 atom % D) using JEOL PMX-60 and GSX-400 spectrometers.

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