Graft Copolymerization Studies. III. Methyl Methacrylate onto Polypropylene and Polyethylene Terephthalate

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ABSTRACT: The *tert*-butoxy radical-facilitated grafting of methyl methacrylate (MMA) onto commercial polypropylene (PP) pellets and fiber was investigated in heterogeneous conditions similar to practical systems. Free-radical grafting of several other monomers onto PP fiber was also investigated. Also, preliminary data from the grafting of MMA onto poly(ethylene terephthalate) pellets is presented. The PP-graft-PMMA residues were detected by solid-state ^{13}C-NMR and photoacoustic IR spectroscopy. There was a good correlation between the degree of grafting (DG) determined from these spectroscopic techniques and the results from gravimetric methods. A maximum grafting efficiency of over 50% was found, whereas DG (20%) remained constant at various PP pellet, initiator, and monomer concentrations. However, at relatively low PP fiber concentrations, the DG was 27%; the increase was most likely due to the greater surface area of the fiber. There was also a reduction in DG (14%) at relatively low initiator concentrations. The reaction conditions were altered to favor grafting by the addition of more polymer substrate. When the ratio of *tert*-butoxy radicals to PP was decreased, more of the substrate remained unmodified, and empirical calculations showed the formation of grafts with up to 40 monomer units. At high initiator concentrations, calculations showed that the graft residues were 1–2 units long. Therefore, variation of the polymer, initiator, and monomer concentrations was shown to have a significant effect on grafting. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 898–915, 2002

Key words: graft copolymers; poly(propylene); NMR; FTIR

INTRODUCTION

Because of their inherent nonpolar nature and lack of functionality, polyolefins and polyesters are very resistant to chemical bonding on their surfaces. This limitation can be overcome by free-radical-initiated grafting of polar vinyl monomers onto the polymers, a method readily applied in many existing industrial processes.[1,2] We previously reported[3,4] on the reactions of small molecules toward *tert*-butoxy radicals to obtain data that could be applied to free-radical-facilitated graft copolymerization and the conditions necessary to maximize the amount of graft residue obtained. This study included the use of 3-methylpentane and 2,4-dimethylpentane as models for linear low-density polyethylene (LLDPE) and polypropylene (PP), respectively.[3] Studies have also been conducted with a mixture of ethylene glycol dibenzoate and diethylene glycol dibenzoate as a model for poly(ethylene terephthalate) (PET).[4]

Preliminary studies performed in our laboratories have shown that it is possible to graft methyl methacrylate (MMA) onto hydrocarbons, such as

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3-methylpentane, with *tert*-butoxy radicals.[3] These radicals were chosen because they exhibit enhanced propensities for hydrogen abstraction[5–7] compared to other primary radicals[8] over the addition to monomer, which suggests that grafting could be competitive with unwanted homopolymerization. Of the monomers investigated, it was also determined that MMA might give more graft residue.[3] The reaction kinetics can also be altered to favor grafting through an increase in the substrate concentration. Through the decrease of the ratio of *tert*-butoxy radicals to 3-methylpentane, more of the substrate remains unmodified.[3] The results of the 3-methylpentane study were equally applicable to those of other model compounds.[3,4]

Extending the data from the model studies to polymers, it was proposed that LLDPE would give more grafting than PP because of its greater reactivity toward *tert*-butoxy radicals.[3] However, there is evidence in the literature to suggest the possibility of unwanted LLDPE crosslinked products during free-radical-initiated graft copolymerization.[9,10] Because the formation of crosslinked products would complicate the study, this investigation focused on *tert*-butoxy-radical-initiated grafting of MMA from PP.

This article reports on the effect of PP, initiator, and monomer concentrations on the *tert*-butoxy-radical-facilitated grafting of MMA onto PP pellets and PP fiber in heterogeneous conditions. Evidence for the grafting of MMA onto the polyolefin is presented. The effect of the choice of initiator and of monomer used in polymerization was also studied. Preliminary data from the free-radical-initiated grafting of MMA onto PET pellets is presented. The significance of these results for radical-facilitated grafting of PP and PET is also discussed.

EXPERIMENTAL

Instrumentation

Solution-state ^{1}H-NMR spectra were recorded at 399.8 MHz with a Varian Unity Plus 400 spectrometer (Palo Alto, CA) and with $CDCl_3$ as the solvent. Solid-state ^{13}C-NMR experiments were performed on a Varian Unity Plus Inova 300 MHz spectrometer (Palo Alto, CA), with a Doty SiN rotor and Kel-F caps, using cross polarization–magic angle spinning (CP–MAS) and high-power dipolar decoupling techniques. The experiments were accumulated at a spectral width of 30,000 Hz, a relaxation delay of 3.0 s, and an acquisition time of 0.017 s.

Fourier transform infrared (FTIR) photoacoustic spectroscopy was performed with a Biorad FTS-60A spectrometer (Hercules, CA) with a MTEC Model 200 photoacoustic detector (Ames, IA) purged with a steady flow of helium gas before measurement. The samples were recorded as solids, and for each sample, 64 scans were collected at a resolution of 2 cm^{-1}. The data was analyzed with Grame Research software (Galactic Industries Corporation, Salem, NH).

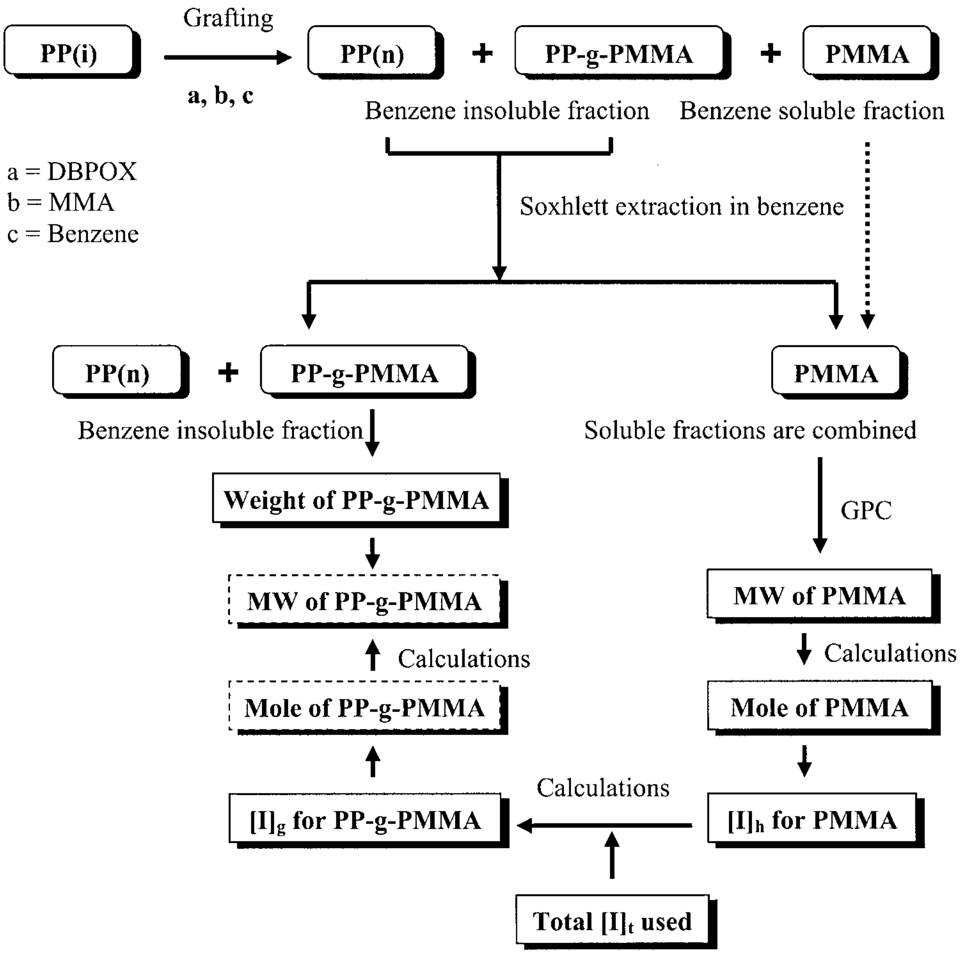
Gel permeation chromatography was performed with a Waters instrument (Milford, MA) equipped with a model 510 pump and 410 differential refractometer. Three Waters Styragel columns were used in series (HR1, HR2, and HR3). The columns were placed inside a column box maintained at 30°C. The eluant, tetrahydrofuran (high performance liquid chromatography [HPLC] grade), was used as received. The solvent flow rate was maintained at 1.0 mL/min. Data was analyzed with the BASELINE software package from Waters. The polymer–solvent system was calibrated with the log of the molecular weight, expressed as a linear relationship of the elution volume based on five polystyrene standards (TOSOH Corp., Yamaguchi, Japan) with molecular weights between 450 and 37,900.

Materials

PP pellets and PP fiber (Milestone Chemicals Proprietary Ltd., Victoria, Australia) and PET pellets (Aldrich, Milwaukee, WI) were washed in refluxing benzene for 24 h and then dried under vacuum before use. Di-*tert*-butyl peroxalate (DBPOX) was prepared by the method of Bartlett et al.[11] Azobis isobutyronitrile (AIBN) was purified by recrystallization twice from methanol. The monomers (Aldrich) MMA, 2-hydroxyethyl methacrylate (HEMA), 2-dimethylamino ethyl methacrylate (DMAEMA), allyl methacrylate (AMA), methyl acrylate (MA), methacrylonitrile (MAN), styrene (S), 4-vinylpyridine (4VP), and vinyl acetate (VAC) were passed through a plug of basic alumina and distilled immediately before use. Maleic anhydride (MAH) and benzene (Aldrich) were used as received.

General Procedure for Grafting

Solutions of DBPOX and MMA in benzene (5 mL) were added to PP (pellets or fiber) (Scheme 1).



Scheme 1 Grafting process, which includes separation of the benzene-soluble and benzene-insoluble fractions, and the calculation of $[I]_g$ and the molecular weight of the graft-PMMA chain.

Solutions of DBPOX with a series of different monomers (in benzene) were also added to PP fiber. The heterogeneous reaction mixtures were degassed by successive freeze–pump–thaw cycles on a reduced-pressure vacuum line[12] and then were heated at 60°C (±1°C) for 70 min (10 initiator half-lives).[11] Polymerizations were also performed with AIBN as the initiator (0.85 mmol). The reaction mixtures were heated at 60°C (±1°C) for 72 h (10 initiator half-lives).[13]

At the completion of the experiment, the reaction vessel contained benzene-soluble and benzene-insoluble material. The soluble solution was removed by trituration and found to contain exclusively polymethyl methacrylate (PMMA) by ^{1}H-NMR spectroscopy. The benzene-insoluble material was extracted in refluxing benzene to remove any remaining homopolymer. The benzene-soluble fractions were then combined and concentrated under reduced pressure to obtain low-molecular-weight PMMA as a viscous oil, and the mass was determined gravimetrically (see Scheme 1). The benzene-insoluble material contained a mixture of PP and PP-graft-PMMA that was not separated because the samples were not readily soluble in common organic solvents. The mixture was dried under vacuum, and the mass was determined by gravimetric methods. Similar experimental conditions were used to graft MMA to PET (pellets) with DBPOX as the initiator.

There was no change in the appearance of the grafted polymer samples. However, quantitative spectroscopic experiments carried out on different portions of the grafted material showed that the grafts were distributed evenly on the surface of the polymer substrate.

Analysis of the Graft Yields

Determination of the Mass of Graft-PMMA

The mass of graft-PMMA was determined from the weight difference of the original polymer, for example, PP or PET, before and after polymerization, which included trituration and soxhlet extraction to remove all traces of the homopolymer (see Scheme 1).

$$\text{Graft-PMMA} = \text{Benzene-Insoluble Fraction} - \text{Initial Weight of PP} \quad (1)$$

The total mass of the original polymer did not change during polymerization. Therefore

$$\text{Graft-PMMA} = [\text{PP}(n) + \text{PP-graft-PMMA}] - [\text{PP}(i)] \quad (2)$$

where PP(i) is the PP added initially to solution and PP(n) + PP-graft-PMMA is the benzene-insoluble material that could not be isolated separately, of which PP(n) did not contain any graft residue.

Extent of Grafting

The extent of grafting onto the original polymer, for example, onto PP or PET, was defined with the following parameters[14]:

$$\text{Degree of Grafting (DG)} = \frac{\text{Mass of Graft-PMMA}}{\text{Mass of PP}(i)} \times 100 \quad (3)$$

$$\text{Grafting Efficiency (GE)} = \frac{\text{Mass of Graft-PMMA}}{\text{Mass of Graft-PMMA} + \text{Mass of PMMA}} \times 100 \quad (4)$$

With these definitions, it is possible to express the graft-PMMA as a percentage function of the mass of PP (or PET) used during polymerization and the total amount of MMA consumed by competing graft and homopolymer reactions.

Determination of the Moles of Initiator Consumed Through Grafting and the Molecular Weight of Graft-PMMA Chains

In this study, the number of moles of *tert*-butoxy radicals consumed through grafting and the molecular weight of the graft-PMMA residue was calculated indirectly from the homopolymer data (eq. (5),[15] (see Scheme 1). This approach was used because the polymer-graft-PMMA samples were not readily soluble in common organic solvents. Therefore, it was not possible to determine the number-average molecular weight of the graft residues with traditional analytical techniques.

$$f = \frac{\{[n(\text{PMMA}) + n(\text{Graft-PMMA Residue})] \times \text{Conversion Constant}\}}{N \times n(\text{Initiator})} \quad (5)$$

where f is the initiator efficiency, n is the number of moles, and N (=2) is the number of *tert*-butoxy radicals generated per initiator molecule. The conversion constant (1.4) is used to convert between moles (e.g., PMMA) and the moles of initiator consumed, for example, through homopolymerization ($[I]_h$).

In this study, f was assumed to be 1 because the *tert*-butoxy radicals were almost entirely consumed by the competing hydrogen abstraction and monomer initiation reactions. The use of small molecules as model compounds for the polymers showed that only 3–8% β-scission-derived products were formed in the presence of MMA.[3,4] This suggests that *tert*-butoxy radical β-scission, to form methyl radicals and acetone, was a relatively minor reaction pathway. Studies have also shown that the combination of *tert*-butoxy radicals to yield $(CH_3)_3$—C—O—O—C—$(CH_3)_3$ is of little significance.[16] Polymerizations were also carried to about 100% initiator decomposition, although f could decrease with conversion due to an increase in the importance of cage reactions.[17]

Studies have shown that the k_{td}/k_{tc} ratio in PMMA termination is about 1.3 (60°C),[18,19] where k_{td} and k_{tc} are the disproportionation and combination termination-rate coefficients, respectively, which equates to about 60% disproportionation. There has been, however, a considerable discrepancy in the precise values of k_{td}/k_{tc}.[20] In some cases, the difference has been attributed to the failure to allow for other modes termination under the polymerization conditions, for example, primary radical termination.[21] Termination exclusively by combination is expected to yield two initiator end groups (I) per molecule (i.e., I-PMMA-I). The conversion constant, therefore, equals 2 minus the disproportionation percentage (or $2 - 0.6$, where 0.6 equals the percent disproportionation).

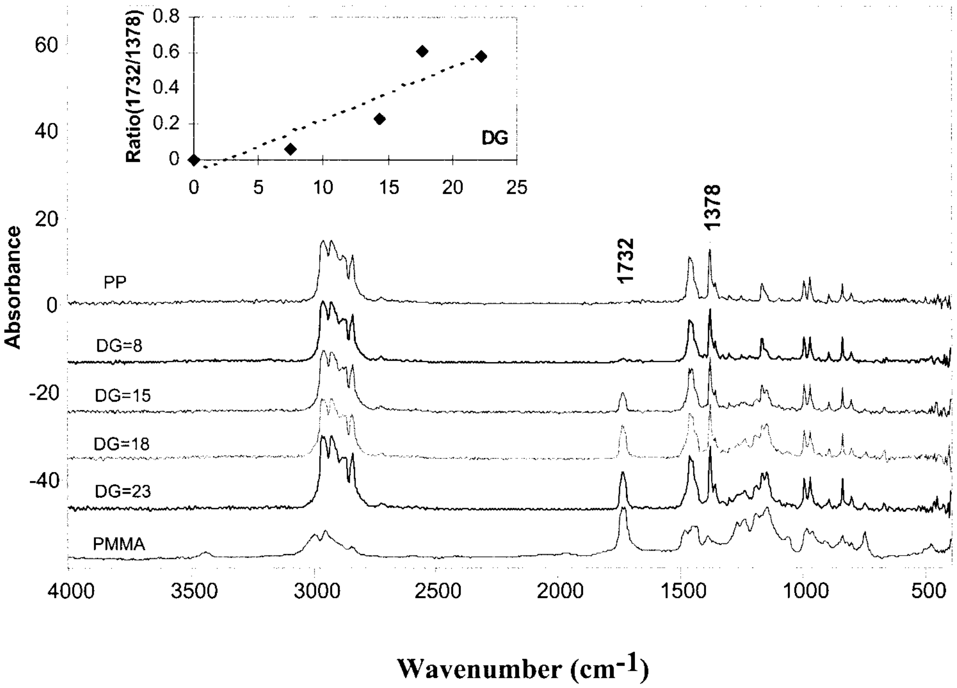


Figure 1 FTIR photoacoustic spectra of PP pellets with variable DG and PMMA homopolymer and the plot of the ratios of the peak heights of the 1732 cm^{-1} band to the 1378 cm^{-1} band versus DG (inset). The absorption at 1378 cm^{-1} was due only to PP, whereas the absorption at 1732 cm^{-1} was due only to PMMA residues.

In applying this constant value, we made the assumption that the graft-PMMA chains terminated by the same mechanism as the homopolymer (i.e., mixture of disproportionation and combination). However, there existed the possibility of primary radical termination between the graft-PMMA radical chains with either the *tert*-butoxy radicals or PP radicals, which is discussed in more detail later.

The initiator consumed through grafting ($[I]_g$) and, hence, the moles of graft-PMMA were calculated indirectly from $[I]_h$ and the total amount initiator used in the reaction. The polymer radical concentration (i.e., PP and PET) was equal to $[I]_g$ because each initiator radical generated a carbon radical that could initiate grafting. The molecular weight of graft-PMMA was then determined from the calculated moles of graft-PMMA and the mass, which was obtained by gravimetric methods.

RESULTS

The effect of reactants on the *tert*-butoxy-radical-initiated graft copolymerization of MMA onto PP was evaluated through a series of experiments with the extent of grafting as the initial parameter studied. Reactions were performed at various polymer, initiator, and monomer concentrations. For each copolymerization series, there was only a single variable reactant.

Evidence of Graft-PMMA and Determination of DG with Spectroscopic Techniques

Figure 1 shows the FTIR spectra of PP pellets containing varying amounts of grafted PMMA (PP with variable DG). The homopolymer was removed from the PP-graft-PMMA samples prior to characterization (see Scheme 1). Figure 1 also shows the FTIR spectrum of a PMMA homopolymer control sample.

The absorptions at 1732 cm^{-1}, the characteristic signal of the carbonyl functionality of methacrylate grafts,[22] were evidence of graft-PMMA. Also, as the DG decreased, so did the absorption ratio of 1732-over-1378 cm^{-1} (the signal at 1378 cm^{-1} was due only to PP). Therefore, the DG determined by gravimetric methods (i.e., mass difference before and after polymerization; see Materials section) was proportional to the ratios

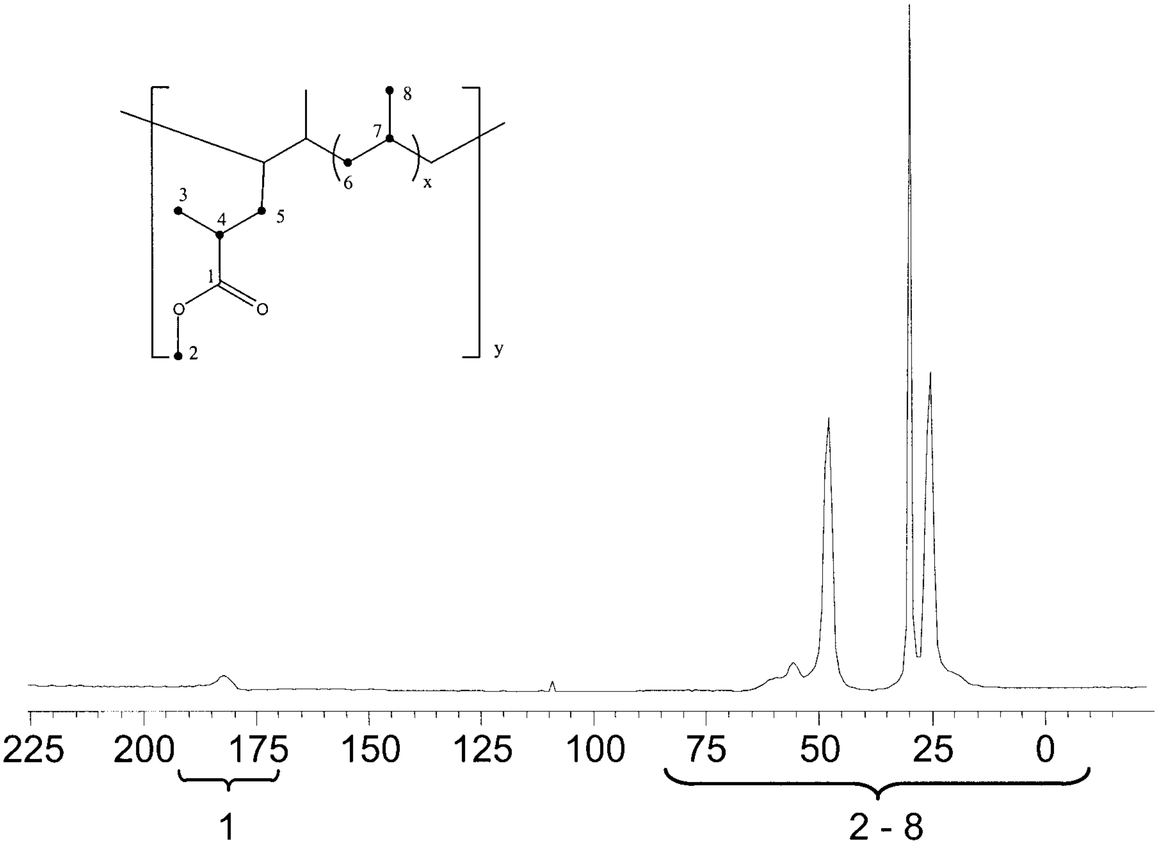


Figure 2 CP–MAS solid-state ^{13}C-NMR spectrum of a mixture of PP and PP-graft-PMMA and the structure of a PP-graft-PMMA repeat unit (inset).

of the peak heights of the 1732 cm^{-1} band to the 1378 cm^{-1} band of the FTIR spectrum (see Figure 1 inset).

Figure 2 shows the solid-state spectrum of a graft-PMMA sample prepared with 1.0 mol/L of PP fiber (Sample A1, see Table I). Similar spectra

Table I Effect of Polyolefin Concentration on the *tert*-Butoxy-Radical-Initiated Graft Copolymerization of MMA from PP Pellets and Fiber

Sample[a]	[PP] (mol/L)	Graft-PMMA Mass (mg)	Graft-PMMA Yield (%)	PMMA Mass (mg)	MMA Consumed Yield (%)
H1	—	—	—	866.4	85.5
A1	1.0	37.5	3.7	755.8	78.8
A2	1.8	85.1	8.4	764.3	83.7
A3	2.8	110.9	11.1	656.1	76.8
A4	5.4	231.3	22.8	605.6	82.8
A5	10.8	418.9	40.8	565.4	95.9
A6	16.2	542.2	52.5	503.2	98.2
B1	1.0	55.4	5.6	781.0	83.9
B2	1.8	80.8	8.1	746.5	83.3
B3	2.8	102.3	10.2	712.0	80.9

The molecular weight of a PP repeat unit [—CH(CH$_3$)CH$_2$—] was 42. [DBPOX] = 0.10 mol/L; [MMA] = 2.0 mol/L.

[a] Sample H1 was the homopolymer reaction. Samples A1–A6 were prepared from reactions in the presence of PP pellets, and B1–B3 were in the presence of PP fiber.

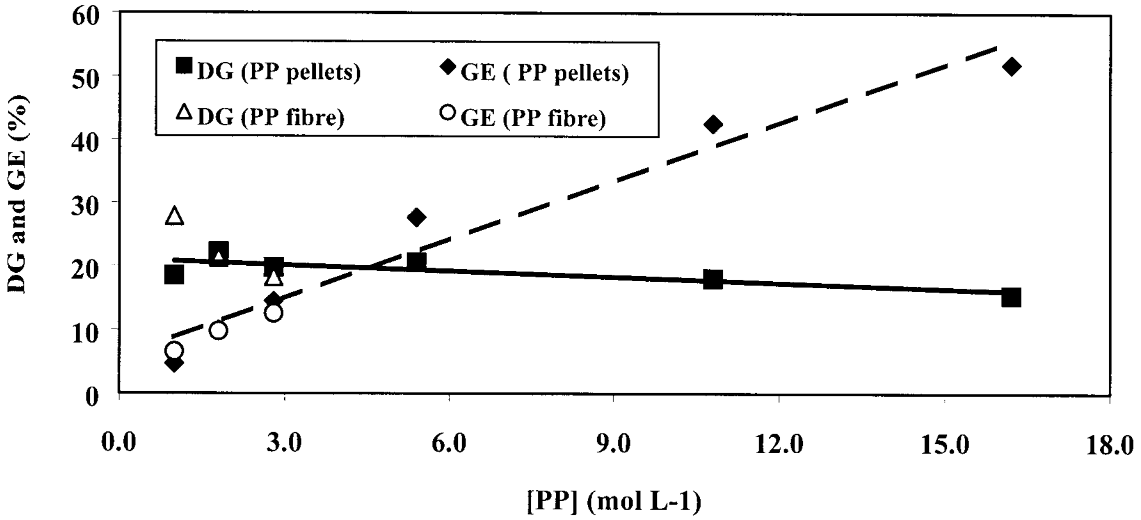


Figure 3 Effect of PP pellet and fiber concentration on the DG and GE.

could not be obtained with PP pellet samples because of poor packing in the instrument thimble, the equivalent of a sample tube in solution-state NMR spectroscopy, due to the unrestricted movement of the pellets in the thimble. The resonance at 181.1 ppm, the characteristic signal of carbonyl functional groups,[23] was further evidence of the presence of graft-PMMA. Other supporting evidence included the overlapping methoxy and methylene carbon signals at 55.1 ppm (broad).[23] The quaternary (47.3 ppm) and methyl carbons (29.4 and 24.7 ppm)[23] were almost entirely swamped by the signals of the PP backbone.

With solid-state ^{13}C-NMR spectroscopy, it was also possible to determine absolute DG data. The DG was determined from NMR measurements by the integration of peak areas. Unlike in the solution state, the solid-state ^{13}C-NMR spectrum was obtained by the use of hydrogen decoupling to the entire molecule, not only to the carbons to which hydrogen(s) were connected. Therefore, integration of carbon absorptions represented the relative amounts of carbon in the structure.

By integration of the solid-state ^{13}C-NMR spectrum, the area of the carbonyl functionality of the PMMA moiety was 4; the area of the remaining carbons was 139. Therefore

$$\text{Carbonyl Carbons : Other Carbons} = 4 : 139$$
$$= 1 : 139/4$$

However, the PMMA moiety contained four carbon atoms, whereas the PP backbone had three carbons (see Fig. 2 inset):

$$\text{PMMA moiety (mol) : PP backbone (mol)}$$
$$= 1 : [(139/4 - 4)/3] = 1 : 10.25$$

Therefore

$$DG_{\text{NMR}} = \text{Weight of PMMA Moiety/Weight of}$$
$$\text{PP Backbone} = (1 \times 100)/(10.25 \times 42) = 23.2\%$$

where 100 is the molecular weight of a repeat unit of MMA and 42 is the molecular weight of the PP repeat unit. The DG value of 23%, obtained by integration of the respective areas of the ^{13}C-NMR spectrum, compared well with the value obtained by the mass difference method (mentioned later).

In addition to providing evidence of the graft-PMMA residues, the previous examples illustrate that techniques such as photoacoustic IR and solid-state ^{13}C-NMR spectroscopy can be used to determine DG data.

Effect of PP Concentration

Table I summarizes the graft-PMMA and PMMA homopolymer data obtained in the presence of varying amounts of PP pellets (Samples A1–A6). Also shown is the data for reactions in the presence of PP fiber (Samples B1–B3).

An increase in the polyolefin concentration gave more graft-PMMA and less of the unwanted homopolymer, which resulted in an increase in the GE (Fig. 3). The competing graft and homopolymer reactions consumed between 80 and 98% of the monomer added to solution, depending

Table II Effect of Monomer Concentration on the *tert*-Butoxy-Radical-Initiated Graft Copolymerization of MMA from PP Pellets

Sample	[MMA] (mol/L)	Graft-PMMA Mass (mg)	Graft-PMMA Yield (%)	PMMA Mass (mg)	MMA Consumed Yield (%)
A7	0.5	69.6	27.2	176.6	96.2
A8	0.8	79.0	21.1	278.3	95.3
A9	1.0	78.4	15.7	376.5	91.0
A2	2.0	85.1	8.4	764.3	83.7
A10	3.6	84.9	4.1	1318.4	68.3

[PP] = 1.8 mol/L; [DBPOX] = 0.10 mol/L.

on the reaction conditions. The graft residue mass was in excess of PMMA on addition of 8 mole equivalents of PP pellets to MMA, and a maximum GE of 55% was obtained, indicating that more than half the added MMA was consumed through grafting. This showed that the reaction conditions could be altered to favor radical-facilitated grafting by an increase in the substrate concentration; however, it was not possible experimentally to add more than an 8 molar excess of PP to MMA without the addition more solvent, which in turn, would alter both the initiator and monomer concentrations. Even though the graft-PMMA mass varied with the polymer concentration, the DG was reasonably constant over the range investigated, and an average value of 19.2 ± 1.8% was calculated. Hence, the mass of graft-PMMA was approximately one-fifth the initial weight of the PP pellets.

The PP fiber concentration range was not as extensive as the pellets because it was not possible to add the same quantities to solution due to the greater surface area of the fiber. At relatively low polyolefin concentrations (Sample B1, see Table I), the DG was 28%, which was higher than the values obtained with PP pellets. The GE was also greater than that found with the same concentration of pellets. This increase may be attributable to the greater surface area of the fiber, although such a conclusion could not be substantiated from this result alone. However, at higher PP fiber concentrations, both the DG and GE data were similar to the values obtained with the pellets.

Effect of Monomer Concentration

Table II summarizes the graft-PMMA and PMMA data obtained in the presence of varying MMA concentrations. The PP pellet and initiator concentrations were kept constant throughout this series of experiments.

An increase in the monomer concentration had little effect on the graft-PMMA residue mass. As a result, the DG was effectively unchanged, and the average DG was calculated to be 20.9 ± 1.8% (Fig. 4). As expected, the lower the MMA concentration was, the less homopolymer was produced. Hence, at relatively low monomer concentrations, the GE was as high as 30%. Also at low MMA concentrations, there was very little monomer that was not consumed by the competing graft and homopolymer reactions.

The sample FTIR spectra from this polymerization series exhibited an absorption at 1732 cm^{-1}, which was characteristic of the carbonyl functional group of the graft-PMMA residue (the FTIR spectrum is not shown).[22] The homopolymer was removed from the graft samples prior to characterization (see Scheme 1). Also, the ratios of the peak heights of the 1732 cm^{-1} band to the 1378 cm^{-1} band of the FTIR spectrum remained constant over the MMA concentration range, again illustrating that the DG determined by mass difference was proportional to the height of the appropriate FTIR absorption signals.

Effect of Initiator Concentration

Table III summarizes the graft-PMMA and PMMA data obtained in the presence of varying DBPOX concentrations. The PP and MMA concentrations were kept constant throughout this series of experiments.

Less homopolymer was produced at the lower initiator concentrations. The variable ratio of hydrogen abstraction to monomer initiation for this

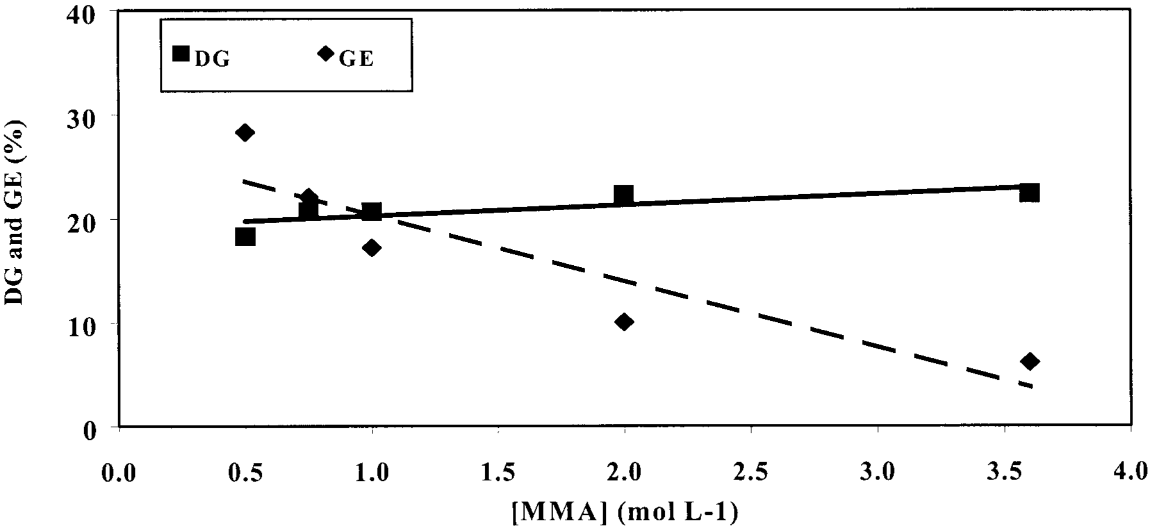


Figure 4 Effect of MMA concentration on the DG and GE.

series of experiments suggested initiator concentration dependency, which was consistent with initiator adsorption into the substrate. Therefore, in heterogeneous reactions, the initiator was distributed between the dispersed and continuous phase. In contrast, the abstraction-to-initiation ratio was expected to be independent of the initiator concentration if the chemistry was occurring in solution with the initiator facilitating abstraction from the substrate.

The maximum GE was 10% for this series of experiments. The addition of 0.6 mol/L of initiator (Sample A15) gave less graft compared to polymerizations conducted at lower concentrations, where there was little effect on the mass of graft-PMMA produced. The DG was 14.2%, compared with the average DG calculated for Samples A2 and A11–A14 (21.0 ± 1.3%), (Fig. 5). The ratios of the peak heights of the 1732 cm^{-1} band to the 1378 cm^{-1} band of the FTIR spectrum, previously described as being proportional to the DG, was reduced by a similar amount for Sample A15 for the drop in the DG.

Effect of the Choice of Initiators

The choice of initiator was investigated by the use of AIBN to initiate grafting of MMA from PP fiber. The reaction conditions were chosen such that the polymerizations are carried to about 100% initiator decomposition[13] for the experiments initiated with DBPOX.

The addition of a 1.3 molar excess of PP fiber to MMA gave a 1.1% graft yield and a DG of 1.9%, which was significantly less than observed for polymerizations conducted in the presence of *tert*-

Table III Effect of Initiator Concentration on the *tert*-Butoxy-Radical-Initiated Graft Copolymerization of MMA from PP Pellets

		Graft-PMMA			
Sample	[DBPOX] (mol/L)	Mass (mg)	Yield (%)	PMMA Mass (mg)	MMA Consumed Yield (%)
A11	0.06	74.5	7.4	646.5	71.7
A2	0.10	85.1	8.4	764.3	83.7
A12	0.25	81.4	8.1	899.6	97.7
A13	0.30	73.2	7.2	859.5	91.7
A14	0.40	85.8	8.3	912.8	97.0
A15	0.60	53.8	5.3	894.3	93.0

[PP] = 1.8 mol/L; [MMA] = 2.0 mol/L.

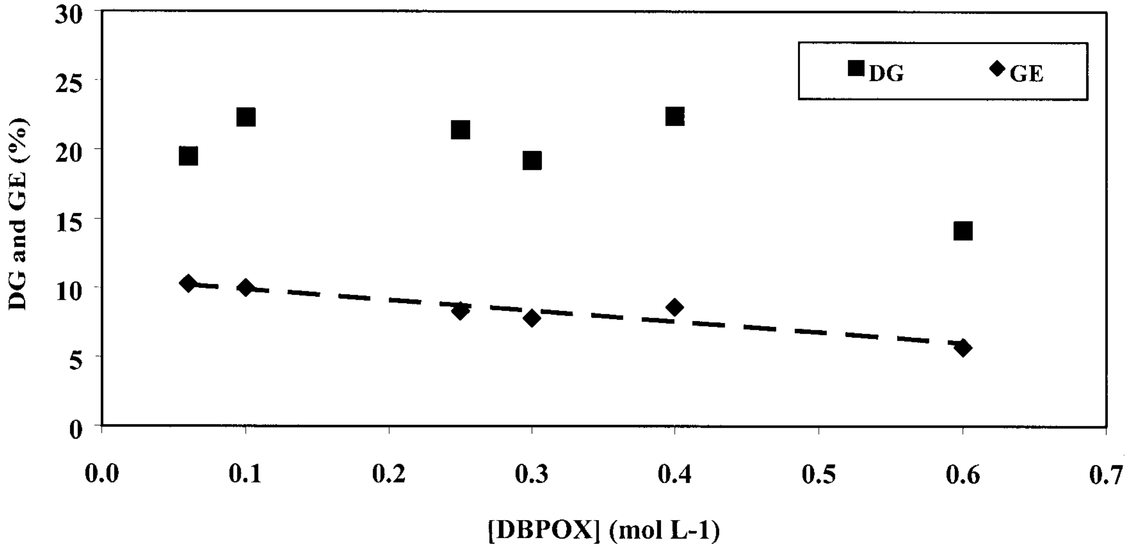


Figure 5 Effect of DBPOX concentration on the DG and GE.

butoxy radicals (cf. Sample B1; see Table I). This suggests that homopolymerization was the more competitive reaction in the presence of AIBN. The likely explanation was that cyanoisopropyl radicals (from the decomposition of AIBN) did not readily facilitate hydrogen abstraction[8]; some grafting may have occurred by intermolecular chain abstraction between the growing homopolymer radical and PP.[24] The greater quantities of graft-PMMA obtained in the presence of *tert*-butoxy radicals suggest that an alternative reaction path was followed. It was most likely that grafting occurred through primary-radical-initiated abstraction from the substrate, generating carbon radicals on the polymer surface,[25] which could then initiate addition to the monomer.

Effect of the Choice of Monomers

Figure 6 shows the DG data for the *tert*-butoxy-radical-initiated graft copolymerization of several vinyl monomers onto PP fiber. Of the monomers investigated, the extent of grafting was highest for the alkyl methacrylates (DMAEMA was the only exception). In the presence of HEMA, the DG was greater than 30%, and the DG was margin-

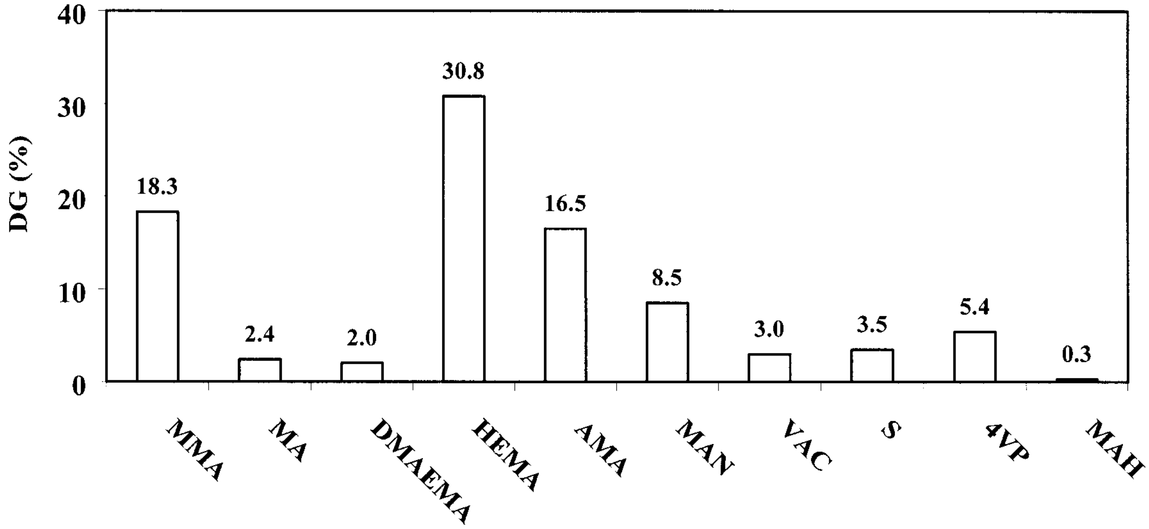


Figure 6 Effect of different types of monomers on the DG.

Table IV Effect of Polyester Concentration on the *tert*-Butoxy-Radical-Initiated Graft Copolymerization of MMA from PET Pellets

Sample	[PET] (mol/L)	Graft-PMMA Mass (mg)	Graft-PMMA Yield (%)	PMMA Mass (mg)	MMA Consumed Yield (%)
H1	—	—	—	866.4	85.5
C1	0.8	31.3	3.1	805.0	82.5
C2	1.4	46.1	4.6	757.5	80.7
C3	2.2	76.1	7.6	713.4	78.8
C4	4.4	151.3	15.3	686.5	84.6
C5	13.0	241.6	23.8	500.1	73.1

The molecular weight of a PET repeat unit [—$OC(O)C_6H_4C(O)OCH_2CH_2O$—] was 208. [DBPOX] = 0.1 mol/L; [MMA] = 2.0 mol/L.

ally under 20% for both MMA and AMA. The GE was also relatively high in the presence of these monomers (approximately 12%). Reactions performed in the presence of the remaining monomers gave DG values less than 10%. Of these, MAN was the highest (~ 8.5%), whereas the DG was between 2 and 6% for most of the other monomers, and MAH gave less than 1%. The GE was very low for these monomers, with the exception of MAH, which did not homopolymerize (GE = 100%), (see Comparison of Different Monomers section).

Grafting of MMA to PET and Its Concentration Effects

The effect of PET concentration on the *tert*-butoxy-radical-initiated graft copolymerization of MMA to the polyester was evaluated through a series of experiments with the extent of grafting as the initial parameter studied. Table IV summarizes the graft-PMMA and PMMA data obtained in the presence of varying amounts of PET pellets.

An increase in the polymer concentration gave more graft-PMMA and less PMMA, which resulted in an increase in the GE, similar to the polymerizations with PP pellets (Fig. 7). Once again, this showed that the reaction conditions could be altered to favor radical-facilitated grafting by an increase in the amount of substrate. However, it was not possible to add more than a 13.0 mol/L of PET. In this study, the maximum GE was 35%, which was lower than the value reported in the presence of PP pellets. The average DG was 3.3 ± 0.5%, also less than previously found with PP.

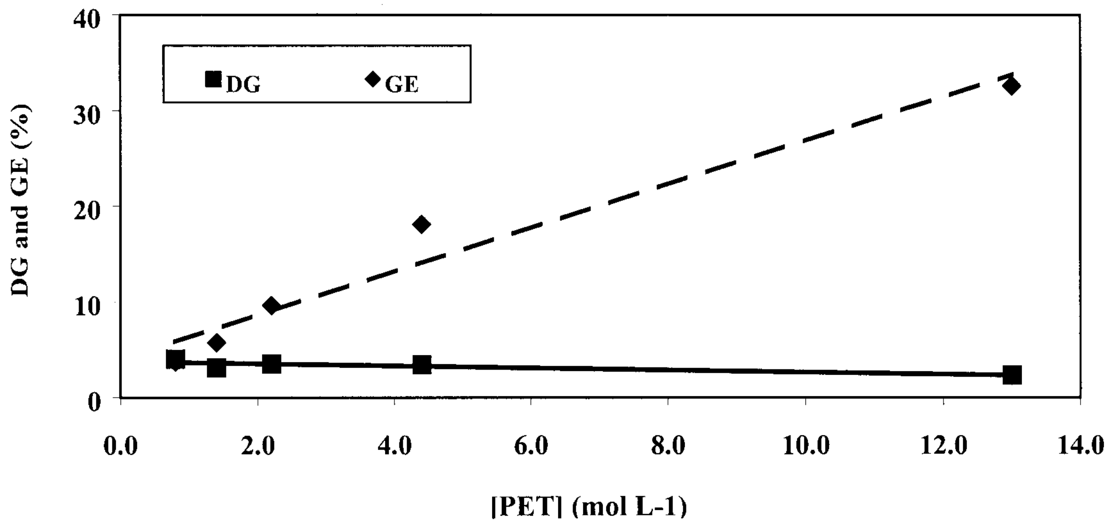
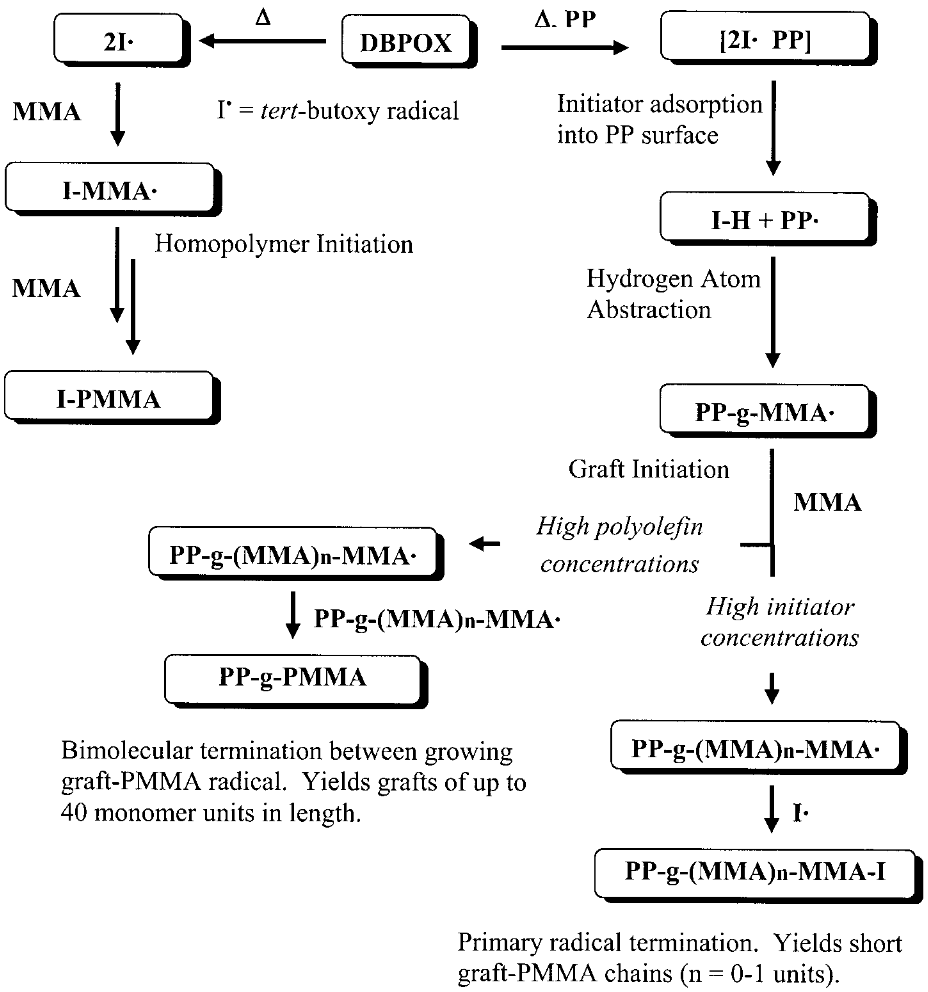


Figure 7 Effect of PET pellet concentration on the DG and GE.



Scheme 2 Competing homopolymer and grafting reactions, including the length of graft-PMMA residues produced at high polyolefin and high initiator concentrations.

DISCUSSION

In this study, MMA was grafted from PP pellets and PP fiber with *tert*-butoxy radicals in heterogeneous conditions similar to practical systems. There have been relatively few studies of the grafting of MMA onto PP with chemical[26] or nonchemical methods[27] reported in the chemical literature. Successful grafting of MMA onto PET pellets in heterogeneous conditions was also reported in this article. Again, relatively few studies using chemical methods have been reported.[28]

Comparison of Model and Polymer Systems

The data reported here shows the successful grafting of PMMA onto PP and PET in heterogeneous conditions with *tert*-butoxy radicals. These radicals were previously used to graft PMMA to 3-methylpentane in homogeneous conditions.[3] The site of grafting to the polymer substrates was previously extrapolated from model studies.[3,4] The most likely mechanism for grafting involved primary radical abstraction from the polymer substrate; the generated carbon radicals then added to the monomer (Scheme 2). The generation of PP radicals and PET radicals was, therefore, an intermediate step in the formation of graft-PMMA residues.

Figure 8 summarizes the PP radical and PET radical concentration data in the presence of varying amounts of the respective polymer substrates. There was an increase in both the PP radical and PET radical concentrations with the addition of the respective polymers as expected.[3,4] The PET radical concentration, how-

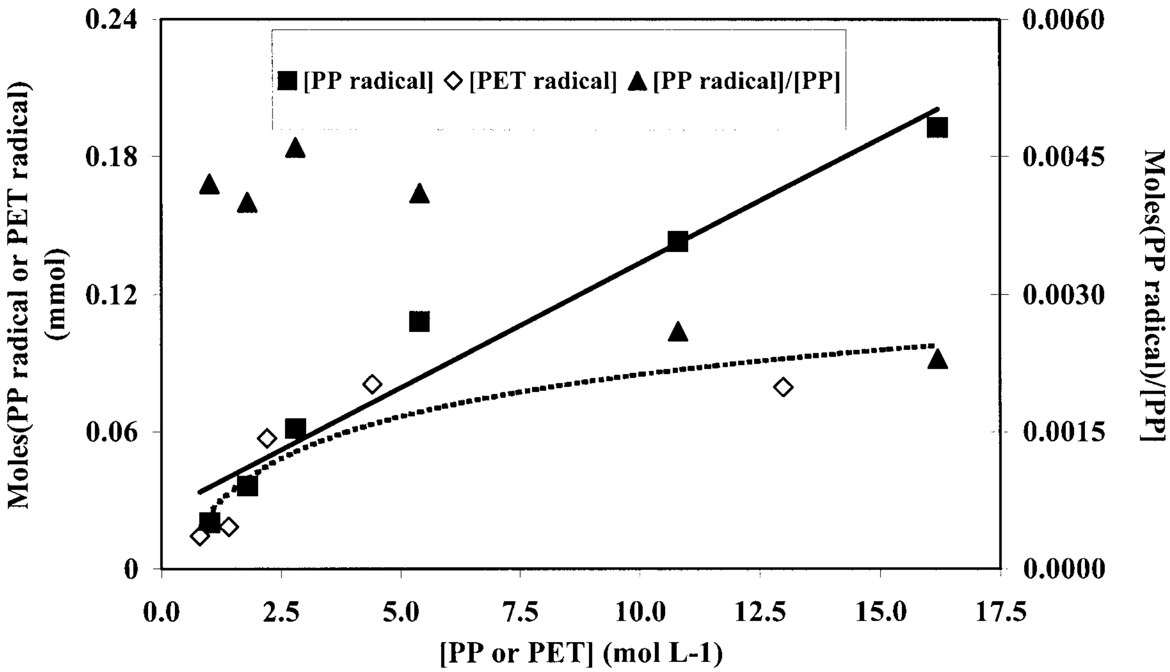


Figure 8 PP radical and PET radical concentrations versus polymer substrate concentration and the concentration ratio of PP radicals to PP (secondary y axis).

ever, appeared to be approaching a plateau. There was a simultaneous reduction in the *tert*-butoxy-MMA radical concentration, which suggested that homopolymerization was less competitive with the addition of more substrate.[3] An increase in the polymer substrate concentration gave more material that was not attacked by *tert*-butoxy radicals, even though higher concentrations of the polymer radicals were produced (see Fig. 8). These results compared well

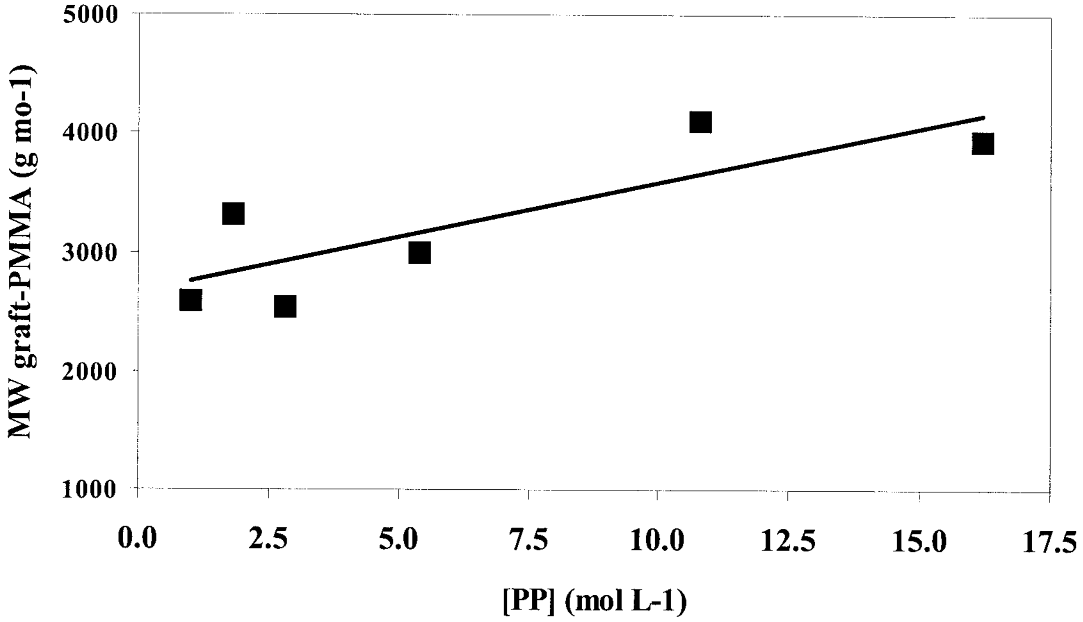


Figure 9 Calculated molecular weight of graft-PMMA residues versus PP pellet concentration.

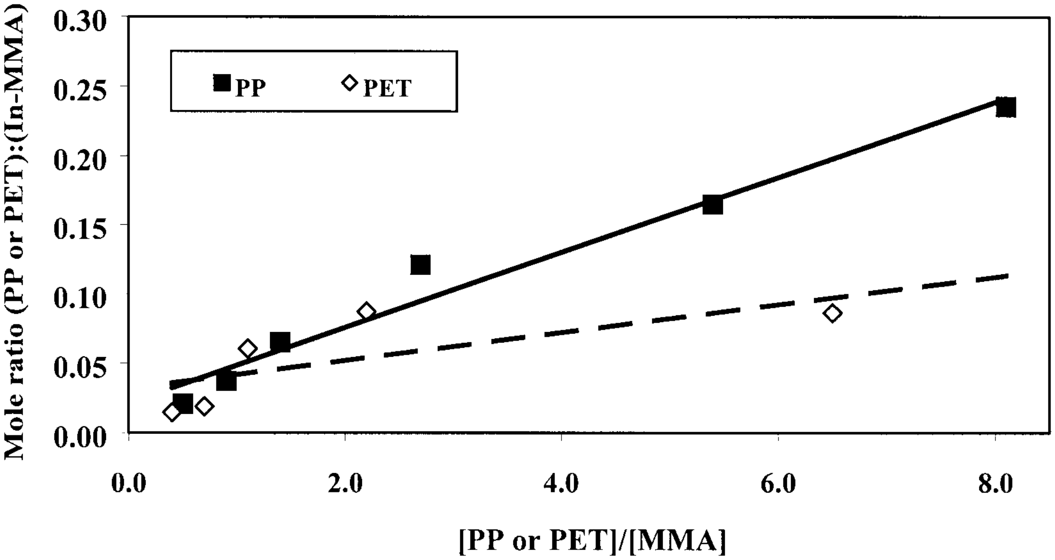


Figure 10 Relative mole ratio of polymer radicals (PP and PET) to initiator–MMA radicals versus polymer substrate to MMA concentration.

with model compound studies.[3,4] There was also an increase in the molecular weight of the graft-PMMA chains with the addition of more substrate (Fig. 9).

In contrast to these results, *tert*-butoxy radicals gave near quantitative hydrogen abstraction yields from the model compounds in the presence of MMA at relatively high hydrocarbon-to-monomer concentration ratios.[3] The difference in reactivity between the models and polymers was more likely due to the greater reactivity of the former toward *tert*-butoxy radicals. Niki and Kamiya reported that polymers, because of their coiled conformations, retard primary radicals from approaching the reaction site and, therefore, are less reactive than small molecules.[29] However, there is no such effect in small molecules.

Relative Rates of Hydrogen Atom Abstraction to Monomer Initiation

The k_a/k_i ratio (where k_a and k_i are the hydrogen abstraction and monomer initiation rate coefficients, respectively) for the polymer substrate and MMA competition reactions was determined from the slope of Figure 10 [Table V, eq. (6)]. Abstraction from PP was almost 2.7 times that from PET, which suggest that PET was less reactive toward *tert*-butoxy radicals. Model compound studies also showed that PET was less reactive; this was attributed to steric factors that reduced primary radical approach.[4] Another contributing factor may by the differences in the surface areas of the respective polymer substrates, although further work needs to be conducted in this regard.

Table V Rates of Abstraction from PP and PET to MMA Initiation: k_a/k_i Ratios

Polymer Substrate	k_a/k_i Ratio
PP	0.024 ± 0.002
PET	0.009 ± 0.001

$$\frac{\text{Rate of Abstraction}}{\text{Rate of Initiation}} = \frac{k_a(I)(\text{PP or PET})}{k_i(I)(\text{MMA})} = \frac{\text{Moles of PP or PET Radicals}}{\text{Moles of In-MMA Radicals}} \quad (6)$$

where I is the *tert*-butoxy radical and In is the *tert*-butoxy end group.

Effect of the Variation of Reaction Conditions on the PP Radical Concentration and Molecular Weight of Graft-PMMA Chains

Figure 11 summarizes the PP radical concentration data at varying initiator concentrations. Increasing the amount of DBPOX had a greater effect on the PP radical concentration compared to varying the amount of polymer substrate (cf.

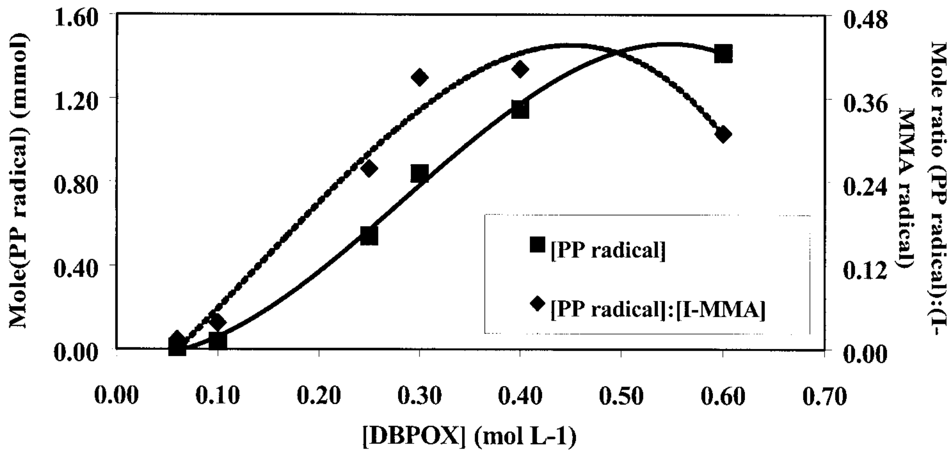


Figure 11 PP radical concentration and mole ratio [PP radicals] : [I–MMA radicals] (secondary *y* axis) versus DBPOX concentration.

Fig. 8). The addition of 0.40 mol/L of DBPOX resulted in almost half of the *tert*-butoxy radicals facilitating hydrogen atom abstraction. The PP radical concentration appeared to reach a plateau on the addition of 0.60 mol/L of initiator. Because of the faster rate of initiation (compared with hydrogen atom abstraction), there was, therefore, a drop in the k_a/k_i ratio. Hence, less MMA was consumed through grafting, which explained the reduction in the DG (see Sample A15, Table III). Although increasing the *tert*-butoxy radical concentration gave more competitive hydrogen atom abstraction, greater amounts of unwanted PMMA were also formed, which made altering the initiator concentration less favorable than varying the PP concentration. At high initiator concentrations, the results were consistent with the graft-PMMA chains being only 1–2 units long, and although this value was only empirical, it did give a reasonable indication of chain length (Fig. 12).

Figure 13 summarizes the PP radical concentration data at varying MMA concentrations. The PP radical concentration was greatest at low monomer concentrations where competing MMA initiation was less favorable as expected. Under these conditions, graft-PMMA chains were calculated to be 4–8 MMA units long.

Chain Termination Mechanism

As previously discussed in this article, there was an initiator concentration dependency for free-

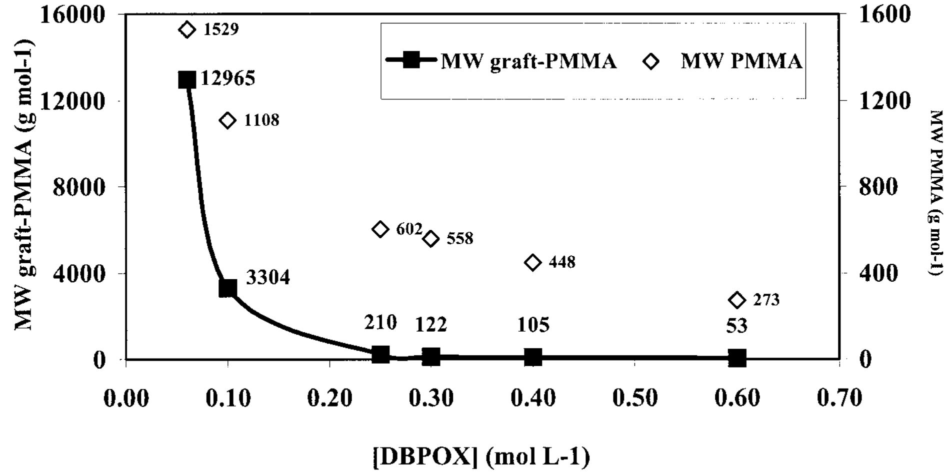


Figure 12 Calculated molecular weight of graft-PMMA residues and PMMA (secondary *y* axis) versus DBPOX concentration.

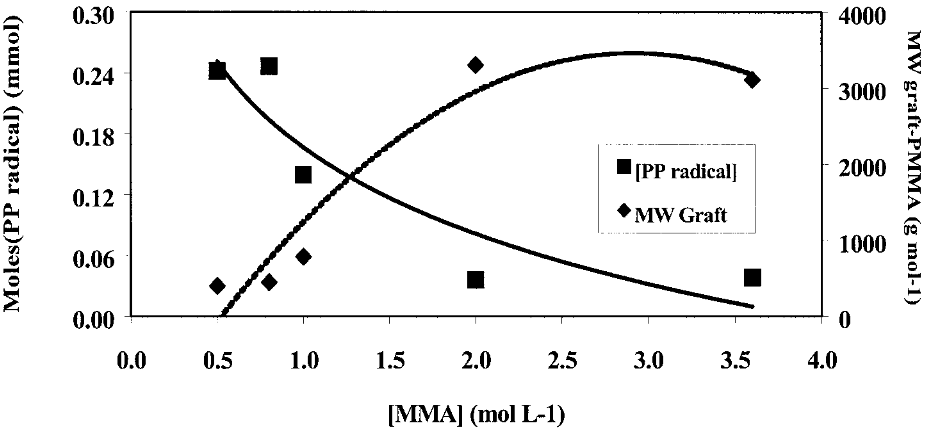


Figure 13 PP radical concentration and the calculated molecular weight of graft-PMMA residues (secondary *y* axis) versus MMA concentration.

radical grafting in heterogeneous conditions, consistent with the initiator being adsorbed into the polymer substrate (see Scheme 2). At high polyolefin (or polyester) concentrations, it was envisaged that more initiator was adsorbed into the polymer surface, which yielded more grafting sites and graft-PMMA chains (see Fig. 8). The reduction in both the homopolymer yield and molecular weight data with increasing substrate concentration was also consistent with the adsorption of more initiator into the polyolefin (see Fig. 12). Chain termination under these conditions would more likely involve bimolecular termination between graft-PMMA radical chains (see Scheme 2).[25,26] The increase in the molecular weight of the graft residues at high polymer substrate concentrations was, thereby, rationalized by the graft-PMMA radical chains, which were not freely mobile, undergoing fewer bimolecular termination reactions (see Fig. 9).

Reactions performed at high initiator concentrations yielded graft-PMMA chains that were 1–2 monomer units in length. It was unlikely that these chains were formed by bimolecular termination between two graft-PMMA radical chains or, alternatively, graft-PMMA radicals with PP radicals (these radicals were not freely mobile). Furthermore, cross-termination between graft-PMMA radical chains and growing homopolymer radicals did not explain the formation of these very short graft-PMMA chains.

Figure 11 shows that there was an increase in the amount of initiator absorbed into the substrate with the addition of DBPOX. The increasing homopolymer yield also suggests that less MMA was available in the surface layer, and therefore, graft propagation was less competitive than termination. The formation of such chains 1–2 units long was, therefore, consistent with primary radical termination between PP-graft-(PMMA)n radicals (where $n = 1$ or 2) and mobile free radicals, most likely to be *tert*-butoxy radicals or methyl radicals (i.e., the β-scission product) as each DBPOX molecule yielded two primary radicals in close proximity (see Scheme 2). The PMMA data also shows that very short homopolymer chains (three units) were formed at relatively high DBPOX concentrations (see Fig. 12).

The data from the AIBN experiment illustrates that cyanoisopropyl radicals did not readily facilitate hydrogen atom abstraction[8]; the low graft yield was attributed to intermolecular chain transfer between the growing PMMA radical and PP.[17] By extrapolation of this result to the graft residues (also carbon centred radicals), termination through intermolecular hydrogen abstraction was similarly not expected to be a significant reaction pathway.

The results shown here illustrate that the graft-PMMA chain length varied with the effective initiator and monomer concentrations in the surface layer of the polymer substrate.

Comparison of Different Monomers

The alkyl methacrylates HEMA, DMAEMA, and AMA were also successfully grafted to PP in heterogeneous conditions. Other types of monomers, such as MA, VAC, S, 4VP, MAN, and MAH, were also grafted to the polyolefin.

Based on the results of previously published competition reactions involving model compounds, monomer, and *tert*-butoxy radicals (in the presence of a radical trap), it was concluded that experiments with MMA would give more grafting than the monomers 4VP and S (which were expected to give the least amount of graft).[3] The more likely reason was that the electrophilic nature of MMA did not favor attack from electrophilic *tert*-butoxy radicals,[30] and therefore, hydrogen atom abstraction from the hydrocarbon substrate was the more competitive reaction.

Other studies have shown that the rate of reaction of *tert*-butoxy radicals toward a series of alkyl methacrylates remains essentially constant.[31] It is, therefore, likely that the initiation rate of these primary radicals towards the alkyl methacrylates, MMA, HEMA, DMAEMA, and AMA would be almost similar. In aromatic solvent, the initiation rates of *tert*-butoxy radicals toward MMA and VAC are the same,[8] whereas initiation to MA is more than twice that found for MMA.[8] In contrast, *tert*-butoxy radicals do not attack MAH.[32] Based on this data, the expected reactivity of *tert*-butoxy radicals toward these monomers was expected to decrease in the following order S > 4VP > MA > MAN > MMA ~ HEMA ~ DMAEMA ~ AMA ~ VAC > MAH.

However, the graft data varied from the expected reactivity based on the relative rates of hydrogen atom abstraction and monomer initiation (see Fig. 6). This suggests that the amount of graft obtained was also dependent on the rates of propagation and termination. For example, the amount of graft obtained in the presence of DMAEMA was significantly less compared to the other alkyl methacrylates. There are reports in the literature that show grafts consisting of single DMAEMA units because of the graft-DMAEMA radical undergoing intramolecular hydrogen abstraction.[14] The importance of intramolecular hydrogen abstraction has also been widely reported for MAH systems.[32] Therefore, MAH grafts were similarly expected to be single monomer units in length.[33–35]

CONCLUSIONS

The results presented in this article demonstrate that MMA was successfully grafted to PP pellets, PP fiber, and PET pellets in heterogeneous conditions with *tert*-butoxy radicals. Significant quantities of MMA-grafts relative to the polymer were achieved with PP (DG = 20%). The ratio of graft-to-polymer substrate was significantly less with PET (DG = 3.5%). Varying the PP, initiator, or monomer concentrations did not have an effect on DG, except at relatively high initiator concentrations and relatively low PP fiber concentrations. However, varying the polymer, initiator, or monomer concentrations was shown to have a significant effect on the chain length of MMA-graft produced. When the ratio of primary radicals to PP was decreased, empirical calculations showed the formation of grafts with up to 40 monomer units. At high initiator concentrations, calculations showed that the graft residues were 1–2 units long.

This article also provides evidence for the characterization of PP-graft-PMMA residues by solid-state ^{13}C-NMR and photoacoustic IR spectroscopy. There was also a good correlation between the DG determined from these spectroscopic techniques and the results from gravimetric methods.

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