

# Grafting kinetics of poly(methyl methacrylate) on microparticulate silica

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(Received 1 November 1989; revised 30 January 1990; accepted 1 February 1990)

Grafting of poly(methyl methacrylate) (PMMA) on microparticulate silica was achieved by initiating the polymerization of MMA by 4,4'-azobis(4-cyanopentanoic acid) that was covalently bound to the silica surface. The initiator seems to be destabilized upon binding it to the silica surface. The kinetics of the graft polymerization are described and are largely affected by the Trommsdorff effect, which makes it possible to graft a high amount of PMMA on silica.

(Keywords: graft polymerization; immobilized radical initiator; 4,4'-azobis(4-cyanopentanoic acid); methyl methacrylate; silica)

## INTRODUCTION

Grafting of polymers on a solid surface is a subject of great interest in a variety of chemical disciplines, e.g. enzyme immobilization<sup>1</sup>, colloid stabilization<sup>2-4</sup>, adhesion in composite materials<sup>5-10</sup>, catalysis<sup>11</sup> and separation studies<sup>12</sup>.

We are especially interested in the promotion of adhesion between fillers and thermoplastic polymers by creating an interlayer consisting of terminally attached polymer chains on fillers like glass particles, interdiffused with a thermoplastic matrix material that is compatible with the immobilized chains.

The thermodynamics of the interdiffusion might be affected by the grafting density and molecular weight of the grafted polymer chains, as predicted by de Gennes<sup>13</sup>. In order to be able to synthesize model systems to study this effect, we undertook a systematic investigation of the grafting kinetics on glass materials like Aerosil, glass spheres, slides, etc., by radical polymerization, initiated by an immobilized initiator.

The model system that will be used is poly(vinyl chloride)/poly(methyl methacrylate) (PVC/PMMA), which is known to be compatible<sup>14</sup>. For this study it is necessary to optimize the grafting reaction to be able to synthesize high grafting densities, which are needed for the model system. This could be accomplished by studying the grafting reaction on Aerosil, because of its high surface area per gram of glass, thus facilitating the analysis of the reaction.

There are three different ways to graft a polymer chain onto a surface, briefly reviewed by Hamann and Laible<sup>2</sup> and Vidal and Donnet<sup>15</sup>, viz. termination of a growing chain on an active group at the surface, copolymerization of an immobilized double bond, and initiation of a polymerization by an immobilized initiator. The last method results in terminally attached polymer chains and also high amounts of polymer can be grafted.

The first radical initiator that is considered to be immobilized is 2,2'-azobisisobutyramidine, irreversibly adsorbed on clay<sup>16,17</sup>. Hamann and coworkers<sup>4</sup> were able to synthesize an aromatic diazo compound chemically attached to a glass surface. Using Aerosil 200 (Degussa) they were able to immobilize  $3.67 \times 10^{-5}$  mol diazo groups per gram of Aerosil, which corresponds to about 4% of the hydroxyl groups originally present. This immobilized diazo group initiated the radical polymerization of a variety of vinyl monomers<sup>4</sup>, in the cases of MMA leading to 1.4 g PMMA/g Aerosil. The kinetics of the graft polymerization of styrene were described in more detail<sup>3</sup>. Other immobilized radical initiators consist, for example, of  $\alpha$ -trichloromethylcarbonyl compounds, from which a chlorine radical is taken off by  $\text{Mo}(\text{CO})_6$  (ref. 7) or by  $\text{Mn}_2(\text{CO})_{10}$  and a photon<sup>18</sup>.

Grafting onto chalk particles was accomplished by adsorbing carbonyl-containing initiators, like the peroxide of succinic acid<sup>6</sup> or 4,4'-azobis(4-cyanopentanoic acid) (ABCA)<sup>5,19</sup>. Finally ABCA could be immobilized on silica materials that were functionalized with  $\gamma$ -aminopropyltriethoxysilane<sup>1</sup>. We have used almost the same approach in order to attach the radical initiator on the glass surface as in that study, by treating the glass surface with an amino-functional silane coupling agent first and consecutively with the acid chloride derivative of ABCA. The thus immobilized initiator (*Figure 1*) has been used for polymerization reactions in solution under different reaction conditions.

## EXPERIMENTAL

### Materials

Silica (Aerosil A200 V, Degussa, average particle diameter 12 nm, specific surface area  $200 \text{ m}^2 \text{ g}^{-1}$ ) was dried overnight at 110°C under vacuum. Toluene and benzene (Merck) were distilled under nitrogen atmosphere from sodium wire/benzophenone before use. MMA (Merck) was distilled under reduced nitrogen pressure

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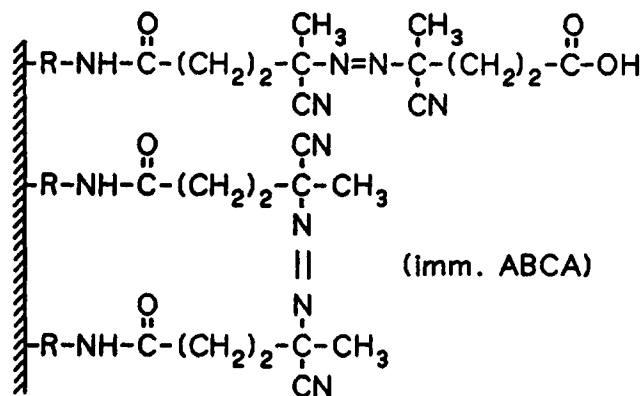


Figure 1 The immobilized radical initiator

from calcium hydride and copper powder and was stored on calcium hydride under nitrogen atmosphere at  $-16^{\circ}\text{C}$ . Aminophenyltrimethoxysilane (APTS, a gift from Dynamite Nobel) was used without further purification, although g.l.c. showed that it consisted of three isomers<sup>20</sup>. Dichloromethane (Merck) was dried on molecular sieves, hexane (Merck) on sodium wire and triethylamine on calcium hydride. Phosphorus pentachloride (Merck) was used as received. 4,4'-Azobis(4-cyanopentanoic acid) (ABCA) (Aldrich) was dried overnight at  $25^{\circ}\text{C}$  under vacuum.

#### Characterization

FTi.r. spectra were recorded on a Bruker IFS 88 spectrophotometer, either by the DRIFT (diffuse reflectance infra-red Fourier transform) technique and converted into absorption spectra using the Kubelka-Munk correction, or by simple transmission measurements of a KBr pellet, as has been indicated in the text.

The molar masses were determined by means of g.p.c. on a Waters ALC/GPC 150 C using tetrahydrofuran (THF) or chloroform as eluent and using polystyrene standards, employing the method of universal calibration. The Mark-Houwink constants used were:  $K=1.12 \times 10^{-4} \text{ dl g}^{-1}$ ,  $a=0.73$  for polystyrene, and  $K=4.8 \times 10^{-5} \text{ dl g}^{-1}$ ,  $a=0.80$  for PMMA eluting with chloroform; and  $K=1.28 \times 10^{-4} \text{ dl g}^{-1}$ ,  $a=0.70$  for polystyrene, and  $K=9.58 \times 10^{-5} \text{ dl g}^{-1}$ ,  $a=0.695$  for PMMA eluting with THF.

The polymer load, the amount of PMMA bound to Aerosil, was determined from elemental analysis; the conversions were determined gravimetrically; and the average surface for one coil ( $S$ ) was calculated from the polymer load ( $P$ ), the number-average molecular weight of the grafted polymer ( $M$ ) and the specific surface area of Aerosil ( $200 \text{ m}^2 \text{ g}^{-1}$ ) using:

$$S = 200 \times 10^{20} / (P/M) N_{av}$$

$S$  has been expressed in  $\text{\AA}^2$  and  $N_{av}$  is Avogadro's number.

The thermal behaviour of the initiators was studied using a Perkin-Elmer DSC II with a scan speed of  $10^{\circ}\text{C min}^{-1}$ . The activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ) from the Arrhenius equation were calculated from the d.s.c. scans using the method of Alberda *et al.*<sup>21</sup>, which was slightly modified in order to study the decomposition of the initiator only. This method calculated the conversion at a certain temperature from the area under the thermogram up to that temperature divided by the total area under the thermo-

gram. The conversion as a function of the temperature could be calculated from one d.s.c. scan. From the conversion the reaction rate constants were calculated assuming the reaction to be first order in initiator. These reaction rate constants gave, in an Arrhenius plot, the activation energy ( $E_a$ ) and pre-exponential factor ( $A$ ), also calculated from one d.s.c. scan.

The melting points of ABCA and 4,4'-azobis(4-cyanopentanoic acid) (ABCC) were checked with a microscope equipped with a small oven.

#### Functionalization of silica

Silica (5 wt%) was suspended in toluene under nitrogen atmosphere. After addition of 2 vol% of APTS, the mixture was refluxed for 3 h and half of the toluene was distilled off. The modified silica was washed with toluene twice, once with ether and was dried overnight at  $110^{\circ}\text{C}$  under vacuum. DRIFT ( $\text{cm}^{-1}$ ): 810 m (Si-O-Si silica), 1110 s (Si-O-Si silica), 1443 w (C-C benzene), 1484 vw (C-C benzene), 1592 vw (C-C benzene), 1602 w (C-C benzene), 1620 w (N-H amine), 3400 m (O-H silica and N-H amine).

Separately a slurry of 40 g  $\text{PCl}_5$  (190 mmol) in 100 ml  $\text{CH}_2\text{Cl}_2$  was added to a suspension of 5 g ABCA (18 mmol) in 50 ml  $\text{CH}_2\text{Cl}_2$  at  $0^{\circ}\text{C}$ . The mixture was stirred overnight under nitrogen while it warmed up to room temperature, the yellow solid was filtered off, 300 ml dry hexane was added and ABCC crystallized at  $0^{\circ}\text{C}$  as a white powder. ABCC was washed with dry and cold hexane and dried *in vacuo* at  $0^{\circ}\text{C}$ , giving 90% yield.

A solution of 7.5 g, ABCC in 100 ml  $\text{CH}_2\text{Cl}_2$  was added dropwise to a suspension of 50 g modified silica in  $\text{CH}_2\text{Cl}_2$  with 4 ml triethylamine over 1 h while the silica was stirred mechanically. After stirring for an additional 2.5 h the silica was centrifuged, washed twice with an acidified water/alcohol (1/1 v/v) mixture, twice with water/alcohol (1/1 v/v), twice with alcohol and twice with ether. The immobilized initiator was dried overnight under vacuum. DRIFT ( $\text{cm}^{-1}$ ): 810 m (Si-O-Si silica), 1110 s (Si-O-Si silica), 1444 vw (C-C benzene), 1484 vw (C-C benzene), 1530 w (N-H amide), 1592 vw (C-C benzene), 1602 vw (C-C benzene), 1672 w (C=O amide), 1710 vw (C=O carboxylic acid), 2943 w (C-H aliphatic), 3400 m (C-H silica and N-H amide).

#### Graft polymerizations

The appropriate amounts of immobilized ABCA, MMA and benzene or toluene were placed in a reaction vessel under nitrogen and heated in an oil bath at a given polymerization temperature for different times.

The grafted polymers were worked up by successive extractions with chloroform/methanol (4/1 v/v) mixtures. One washing procedure consisted of suspending the silica-bound PMMA and centrifuging at an acceleration of  $1.2 \times 10^5 \text{ m s}^{-2}$  for 1 h. Homopolymer that was dissolved in the supernatant liquid was precipitated in a 15-fold excess of petroleum ether 40-60; the liquid was concentrated or diluted if necessary. The washings were repeated until no free polymer was found; in most cases four cycles were enough to wash away all the free polymer. After the last cycle the grafted polymer was suspended in chloroform and poured into 15-fold excess of petroleum ether 40-60. The white powder was dried overnight *in vacuo* at  $70^{\circ}\text{C}$ . The FTi.r. spectrum of PMMA on Aerosil (see Figure 5) is a superposition of

the PMMA spectrum over the Aerosil spectrum. The grafted chains could be removed from the surface by stirring it in a 20% solution of hydrogen fluoride in water for at least 3 days; this procedure breaks down the silica network but leaves the PMMA chains unaltered, as we have tested with a free polymer. The degrafted polymers were washed thoroughly with water, dissolved in acetone, precipitated in petroleum ether 40–60 and dried *in vacuo* at 70°C.

## RESULTS AND DISCUSSION

### The immobilized radical initiator

In the first step of the synthesis of the initiator, Aerosil could be functionalized with  $0.44 \times 10^{-3}$  mol amine groups/g Aerosil, calculated from elemental analysis data. This means that 89% of the hydroxyl groups on the surface have reacted, assuming that one coupling agent molecule reacts with two surface hydroxyl groups<sup>22</sup> and that Aerosil 200 V contains  $1 \times 10^{-3}$  mol hydroxyl groups/g<sup>23</sup>.

Synthesizing ABCC, the slurry of  $\text{PCl}_5$  and ABCA had to be stirred overnight, because shorter reaction times resulted in an incomplete conversion of the carboxylic acid groups. The FTi.r. spectrum of the product after 3 h stirring, as the literature procedure describes<sup>24</sup>, showed three carbonyl bands, a small one at  $1715 \text{ cm}^{-1}$  from unreacted carboxylic acid and two large ones at  $1790$  and  $1810 \text{ cm}^{-1}$  from acid chloride and anhydride respectively. After stirring overnight the FTi.r. spectrum of the product showed only one carbonyl peak at  $1790 \text{ cm}^{-1}$ .

Immobilized ABCA contains  $0.20 \times 10^{-3}$  mol  $-\text{N}$  groups/g silica, also calculated from elemental analysis data, which means a conversion of 90% based on amine groups assuming that one ABCC molecule has reacted with two amine groups on the surface. The DRIFT spectrum of immobilized ABCA (Figure 2) shows the amide absorptions at  $1672$  and  $1530 \text{ cm}^{-1}$ , proving that

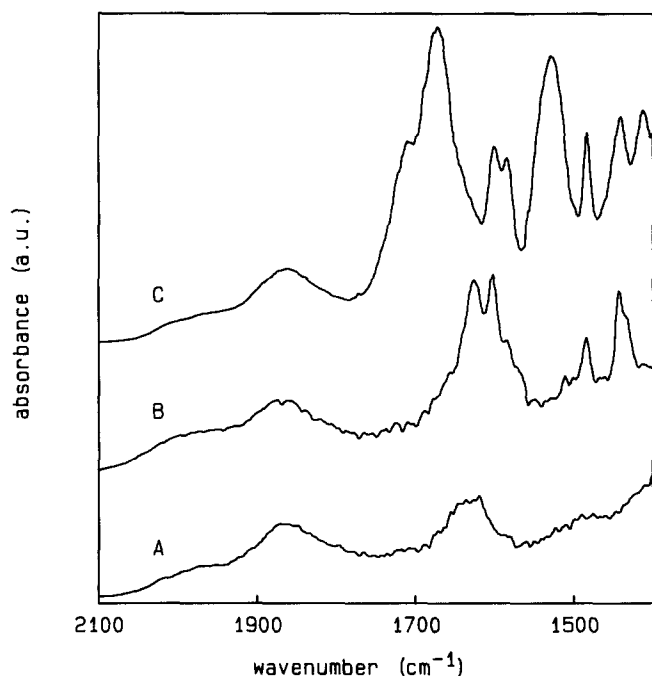


Figure 2 DRIFT spectra of (A) clean Aerosil 200 V, (B) immobilized amine and (C) immobilized ABCA

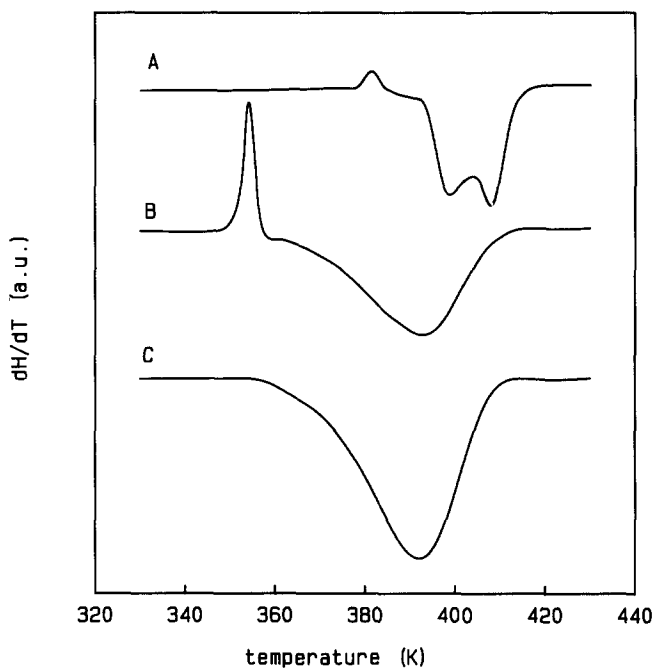


Figure 3 D.s.c. thermograms of (A) ABCA, (B) ABCC and (C) immobilized ABCA

the amide bonds have been formed, but it also shows a small shoulder at  $1710 \text{ cm}^{-1}$ , indicating that some carboxylic acid, formed from the acid chloride during the washing procedures with water, is present. So not all the initiator molecules are linked to the surface by two ends and consequently the conversion mentioned above is somewhat lower than 90%.

We have used d.s.c. to calculate the Arrhenius constants of the decomposition of the radical initiators. Nuyken *et al.*<sup>25</sup> have shown that there is an excellent agreement between this technique and the more conventional ones like u.v. spectroscopy and volumetry. They also showed that the Arrhenius constants of diazo initiators were hardly affected by their physical state. The d.s.c. thermograms of ABCA and ABCC (Figure 3) show endotherms at 110 and 83°C respectively just before the exotherms. These endotherms are likely to be their melting peaks because the melting points are 118 and 80°C respectively. The exotherms are the decomposition peaks, and according to these thermograms it appears that in the dry state the initiators only decompose above their melting points. The exotherm of ABCA appears to be composed of two exotherms but we think it is a small endotherm from the evaporation of water that we could not remove superimposed on a single exotherm from the decomposition of the initiator. This also is the reason for the high experimental error of the value of  $\Delta H$  of ABCA ( $260 \pm 25 \text{ kJ mol}^{-1}$ ). The  $\Delta H$  of ABCC ( $228 \pm 10 \text{ kJ mol}^{-1}$ ) is close to  $\Delta H$  of azobisisobutyronitrile (AIBN) ( $206 \text{ kJ mol}^{-1}$ ) whereas  $\Delta H$  of immobilized ABCA is somewhat higher ( $252 \pm 10 \text{ kJ mol}^{-1}$ ).  $E_a$  and  $\ln A$  were calculated from the linear part of the Arrhenius plot (Figure 4). The non-linear parts of the Arrhenius plot can be ascribed to deviations from normal kinetics because of the beginning or completion of the decomposition of the initiator. Owing to water evaporation effects it was impossible to construct an Arrhenius plot of the decomposition of ABCA. The  $E_a$  of ABCC is nearly the same as  $E_a$  of ABCA published by Popov *et al.*<sup>5</sup> ( $126 \pm 3$  and  $124 \text{ kJ mol}^{-1}$

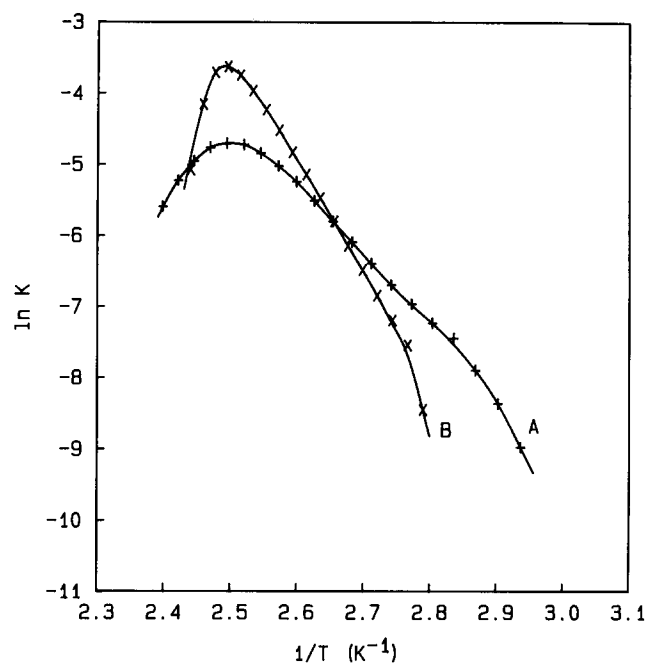


Figure 4 Arrhenius plot of (A) immobilized ABCA and (B) ABCC

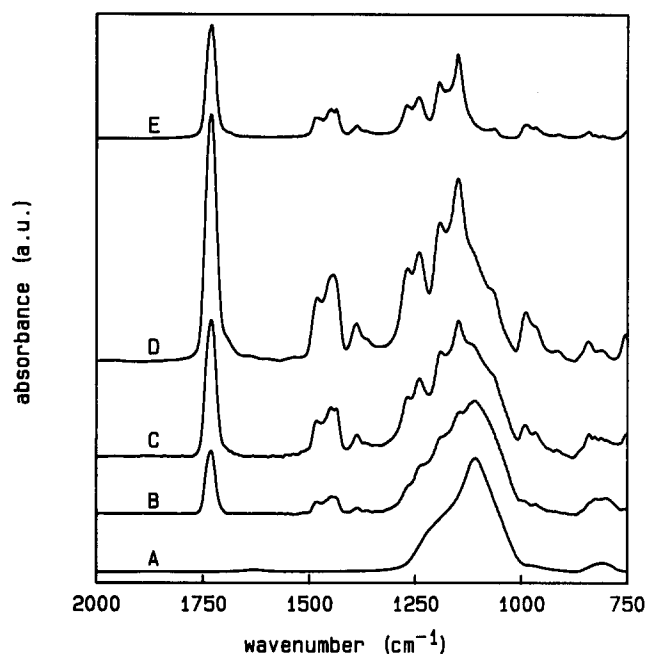


Figure 5 DRIFT spectra after Kubelka-Munk corrections of Aerosil 200 V grafted with (A) 0 g PMMA/g silica, (B) 1.1 g PMMA/g silica, (C) 4.1 g PMMA/g silica, (D) 10.9 g PMMA/g silica and (E) pure PMMA

 Table 1 Polymerizations carried out in 1/1 (v/v) MMA/toluene mixtures at 70°C with an initial initiator concentration of 10.5 mmol<sup>-1</sup>

No.	Reaction time (h)	Polymer load (g PMMA/g silica)	Conversion (%)			$M_n$ (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
1	2	1.6	16	19	35	170	100	3400
2	4	2.9	29	10	39	180	130	2000
3	8	2.7	28	16	44	190	160	2400
4	16	3.4	34	28	63	180	205	1700
5	32	3.8	38	43	81	210	270	1800
6	64	3.8	38	58	96	230	320	1900

respectively). They reported  $E_a$  for ABCA grafted onto  $\text{CaCO}_3$  to be 53 kJ mol<sup>-1</sup> and explained this low value to be due to the presence of the surface, which might affect the stability of the initiator and the ring tension that destabilizes the ground state of the initiator while the transition state is less affected. We have found the same behaviour upon immobilizing the initiator, although  $E_a$  decreased less in our case, i.e. a decrease to  $78 \pm 3$  kJ mol<sup>-1</sup>. This can be explained by the fact that the ring tension should be lower because we have extended the ring by the coupling agent molecules. The initiator molecules that are attached to the Aerosil by one end have no ring tension at all and should behave differently from the initiator molecules with two links to the wall.

#### Graft polymerizations

As can be seen from Figure 5 high amounts of PMMA can be attached to Aerosil; apparently this PMMA is not attached to the silica surface by an adsorption process, because it is known<sup>26</sup> that washing procedures using chloroform/methanol (4/1 v/v) desorb all the PMMA from glass substrates. This has been confirmed in a blank experiment where we have mixed PMMA and Aerosil in this mixture. After centrifuging the Aerosil there were only a few milligrams of PMMA adsorbed on

Aerosil. So the large amounts of PMMA on Aerosil have to be linked covalently to the Aerosil surface.

In an MMA/toluene medium the monomer conversion leading to grafted PMMA increases with longer reaction times but levels off after 16 h (Tables 1 and 2), free PMMA still being formed beyond this point, leading to a total conversion of almost 100%. These observations are in agreement with experiments from Laible and Hamann, i.e. grafting polystyrene onto Aerosil<sup>3</sup>. Their explanations of the steady growth of non-grafted polymer are: first the radical on the Aerosil surface might not be accessible for polymerization whereas the free radical, from the part of the initiator that was attached to the surface by one end, can escape into the bulk and initiate a polymerization, and secondly some of the non-grafted polymer might be formed by thermal polymerization. In our case this latter phenomenon can result from the very small amounts of oxygen that are still present in purified nitrogen gas, for it is known that the thermal polymerization of MMA can be ascribed to peroxides formed after a reaction between MMA and oxygen<sup>27</sup>. It is also very well possible that oxygen has been built in a growing chain, thus forming a peroxide link<sup>28</sup>, which can break open afterwards and initiate another polymerization, although it is known that the re-initiation by the radical chain end is rather slow at 70°C<sup>29</sup>. When this peroxide is situated

**Table 2** Polymerizations carried out in 1/1 (v/v) MMA/benzene mixtures at 70°C with an initial initiator concentration of 1.1 mmol l<sup>-1</sup>

No.	Reaction time (h)	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
7	2	2.1	2	4	6	120	140	1900
8	4	3.2	3	7	10	320	280	3300
9	8	4.7	5	11	16	230	250	1600
10	16	5.1	5	17	22	600	410	3900
11	32	8.6	9	22	31	780	820	3000
12	64	9.6	10	33	43	870	1070	3000

**Table 3** Polymerizations carried out in 1/1 (v/v) MMA/toluene mixtures at 70°C for 8 h

No.	Initiator conc. (mmol l <sup>-1</sup> )	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
3	10.5	2.7	28	16	44	190	160	2400
13	4.4	5.3	23	17	40	675	400	4200
14	1.1	4.1	4	17	21	490	253	4000

**Table 4** Polymerizations carried out in 1/1 (v/v) MMA/toluene mixtures at 70°C for 64 h

No.	Initiator conc. (mmol l <sup>-1</sup> )	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
6	10.5	3.8	38	58	96	230	320	2000
15	5.6	7.0	38	46	84	460	550	2200
16	1.1	7.7	9	31	40	800	810	3500

**Table 5** Polymerizations carried out in 1/1 (v/v) MMA/benzene mixtures at 70°C for 8 h

No.	Initiator conc. (mmol l <sup>-1</sup> )	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
17	8.9	6.3	54	33	87	620	330	3200
18	4.4	6.9	30	14	44	740	450	3600
9	1.1	4.7	5	11	16	230	250	1600

somewhere in a grafted polymer chain, chain scission and subsequent polymerization forms an additional non-grafted polymer chain, thus increasing the amount of non-grafted polymer. Thirdly a non-grafted polymer chain can be formed by a chain transfer reaction from a grafted chain to a (free) monomer or solvent molecule. The two effects mentioned last increase in importance with decreasing initiator concentration.

Tables 1 and 2 show that the molecular weights of grafted and non-grafted polymer increase with longer reaction time, resulting from the Trommsdorff effect<sup>30</sup>. This effect was confirmed by the observation that, between 30 min and 2 h reaction time, the whole medium turned into a macroscopic gel that could no longer be stirred by a magnetic stirrer. As long as initiator is present, it starts new polymerizations. So the number of grafted chains will increase. This means that during the polymerization the surface area for one coil decreases until the initiator is decomposed completely, which is consistent with what we have observed (Table 1). It is noteworthy that the surface area per coil is larger in Table 2 than in Table 1. It appears that the lower initiator

concentration used in the experiments of Table 2 causes higher molecular weights of the polymers. The higher molecular weight of the grafted polymer results in a higher viscosity near the glass surface, leading to a larger fraction of the initiator fragments that recombines without initiating any polymerization. This reduction of the efficiency factor of the initiator leads to a decrease of the number of grafted polymer chains, i.e. an increase of the surface area per coil.

Upon increasing the amount of initiator (Tables 3–6) the polymer loads and the molecular weights go through a maximum. We will discuss this effect later in this section.

Increasing the polymerization temperature above 70°C results in a decrease of the polymer load and molecular weights, as can be seen in Table 7. This is mainly because the rate of decomposition of the initiator increases, resulting in a higher steady-state concentration of radicals and thus a higher rate of radical recombination and chain termination. Furthermore at higher temperatures the viscosity of a polymer solution decreases, so the molecular weights are further decreased by a weaker Trommsdorff

**Table 6** Polymerizations carried out in 1/1 (v/v) MMA/benzene mixtures at 70°C for 64 h

No.	Initiator conc. (mmol l <sup>-1</sup> )	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
19	11.0	6.5	60	40	100	370	420	1900
20	4.5	10.9	48	46	94	610	720	1900
12	1.1	9.6	10	33	43	870	1070	3000
21	0.3	6.5	2	36	38	620	850	3200

**Table 7** Polymerizations carried out in 1/1 (v/v) MMA/toluene mixtures for 64 h with an initial initiator concentration of 1.1 mmol l<sup>-1</sup>

No.	Reaction temperature (°C)	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
22	60	4.8	5	26	31	600	550	3900
16	70	7.7	8	32	40	800	810	3500
23	80	5.1	5	48	53	700	1120	4600
24	90	4.9	5	69	74	360	550	2500

**Table 8** Polymerizations in MMA/toluene mixtures with variable compositions, carried out at 70°C for 64 h

No.	Monomer conc. (vol%)	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
25	20	1.2	33	20	53	170	114	4700
4	50	3.4	34	28	63	180	205	1700
26	80	7.0	46	35	81	690	760	3300

**Table 9** Polymerizations carried out in 1/1 (v/v) MMA/toluene mixtures at 70°C for 64 h

No.	Initiator conc. (mmol l <sup>-1</sup> )	Polymer load (g PMMA/g silica)	Conversion (%)			M <sub>n</sub> (kg mol <sup>-1</sup> )		Surface for one coil (Å <sup>2</sup> )
			Graft	Free	Total	Graft	Free	
16 <sup>a</sup>	1.1	7.7	8	32	40	800	810	3500
27 <sup>b</sup>	1.0	11.2	12	37	49	1590	1580	4700

<sup>a</sup> Under N<sub>2</sub> atmosphere<sup>b</sup> Under vacuum

effect. Moreover the higher rates of chain transfer reactions cause lower molecular weights and thus lower polymer loads. Decreasing the polymerization temperature below 70°C results in a decrease of the polymer load, molecular weights and conversion. Apparently the lower reactivity of the initiator causes a lower conversion and thus a delay of the Trommsdorff effect and so the molecular weight did not reach the value of the polymer prepared at 70°C.

The monomer concentration influences the polymer load on Aerosil, the molecular weights and the conversion very strongly (Table 8). Increasing the MMA concentration causes an increase of the three aforementioned quantities. We can add the result of a polymerization in pure MMA, giving 26 g PMMA grafted per gram Aerosil. The high amount of PMMA on silica made it very difficult to separate the grafted from the homopolymer, so the absolute value of this experiment might be a little questionable but it is in agreement with the trend in Table 8. It is quite clear that the increasing MMA concentration increases the molecular weight of PMMA (normal radical polymerization kinetics), and thus the

polymer load. The higher MMA concentration also causes a higher PMMA concentration after a certain time of reaction, speeding up the Trommsdorff effect, which increases the conversion and polymer load even more.

The effect of oxygen on the polymerization has been indicated in Table 9. The polymer load of the sample prepared under vacuum is higher than that of the sample prepared under nitrogen atmosphere. Schultz and Henrici<sup>28</sup> have shown that an alternating polymer of MMA and oxygen can be formed. Because the oxygen concentration in the purified nitrogen gas is very low, we think that oxygen has been built in the PMMA chain randomly in very small amounts, forming peroxide links. First of all this building-in of oxygen slows down the polymerization reaction because the reactivity of a C-O-O· chain end is much lower than a normal -R· chain end. So the polymerization is somewhat retarded, leading to a lower conversion and polymer load. If oxygen has been built in the polymer chain, the peroxide links formed can decompose afterwards and start new polymerizations at a later stage of the reaction, because they are less reactive than an azo initiator. When the

polymerizations were carried out under vacuum, the oxygen concentration was further reduced and thus also the retardation and re-initiation by peroxides. Apparently chains of PMMA that have been formed after peroxide scission and subsequent initiation are shorter than the pieces that have been formed when there was no oxygen built into the chain, because the molecular weights obtained under vacuum are higher than those under nitrogen. This corresponds to the work of Bamford and Morris<sup>29</sup>, who showed that the rate of decomposition of a peroxide link in a PMMA chain is very low below 90°C, so the polymerization initiated by this peroxide takes place at a late stage of the reaction, in which the monomer concentration is already low so the molecular weight of the newly formed chains is rather small. We have also carried out the polymerization under vacuum with an initiator concentration of 5 mmol l<sup>-1</sup>, which resulted in hardly any differences compared to the polymerization carried out under a nitrogen atmosphere, so only when the initiator concentration is very low (1 mmol l<sup>-1</sup>) does oxygen affect the polymerizations, as could be expected.

The phenomena shown in Tables 3–6 can be explained by the results described above. A decrease of the initiator concentration from 10 to 5 mmol l<sup>-1</sup> leads to higher molecular weight according to normal radical polymerization kinetics, and thus to higher polymer loads on silica. Oxygen hardly affects the polymerization. Decreasing the initiator concentration further makes the effect of oxygen perceptible. The retardation of the polymerization and the slow re-initiation of peroxide links decrease the molecular weights and polymer loads relative to reactions where oxygen has no effect, i.e. reactions carried out with a higher initiator concentration. Also the Trommsdorff effect has its influence. When the initiator concentration becomes too low, the conversion is too small to reach the gel state and thus the Trommsdorff effect does not occur.

## CONCLUSIONS

A new way of immobilizing a radical initiator onto silica substrates was investigated. The initiator was immobilized by an amide bond formed between 4,4'-azobis(4-cyanopentanoic acid) and an amine containing silane coupling agent on the silica, and the presence of the amide bond has been confirmed by FTi.r. The stability of the initiator appears to decrease upon immobilization.

The kinetics of the graft polymerization of MMA on Aerosil are largely affected by the Trommsdorff effect, which is responsible for the higher molecular weights of grafted and non-grafted polymer and thus for the high polymer loads of Aerosil. The Trommsdorff effect was influenced by the initiator concentration, the monomer concentration and the polymerization temperature. Reactions with small initiator concentrations were affected

by very small amounts of oxygen in the nitrogen gas that seem to decrease the polymer load because of the retardation of polymerization and the slow re-initiation of the peroxide links that are thus formed.

## ACKNOWLEDGEMENTS

We would like to express our thanks to the Dutch Ministry of Economic Affairs for financing the Innovation Orientated Research Program, Polymer Composites and Special Polymers (IOP-PCBP), without which this work would not have been carried out. We would also like to thank Professor Dr Hatsuo Ishida for helpful discussions.

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