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HOMOPOLYMERIZATION OF POLY(DIMETHYLSILOXANE) MACROMONOMERS VIA FREE RADICAL POLYMERIZATION

HOMOPOLIMERIZACIÓN DE MACROMONÓMEROS DE POLI(DIMETIL SILOXANO) VÍA POLIMERIZACIÓN POR RADICALES LIBRES

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Abstract

Homopolymers of poly(dimethylsiloxane) terminated with one methyl methacrylate end group (PDMS-MA) were synthesized by conventional free radical polymerization. The crucial step to polymerize the commercial PDMS-MA macromonomers was their purification using a free radical pre-polymerization technique. The separation of homopolymer and unreacted PDMS-MA macromonomer was achieved by precipitation in a mixture of diethyl ether/methanol (1:1). Kinetic studies of homopolymerization yielded the ratio between rate of propagation and termination ($k_p/k_t^{1/2}$). This ratio decreased with increasing the molecular weight of the macromonomers. The apparent rate of propagation was proportional to $[I]^{2.2}$ and $[M]$ for appropriate polymerizations conditions. The ceiling temperature were calculated for macromonomers with $M_n = 1$ and 5 Kg/mol, to be $T_c = 160^\circ\text{C}$ at $[M_1] = 0.88$ and $[M_5] = 0.11$ mol/L, for both homopolymers.

Keywords: Macromonomer, Poly(dimethylsiloxane), free radical polymerization, homopolymerization, purification, pre-polymerization, polymerization, kinetic, ceiling temperature.

Resumen

Los homopolímeros de poli(dimetilsiloxano) con terminación metil metacrilato (PDMS-MA) fueron sintetizados por medio de polimerización de radicales libres. La purificación de estos macromonómeros PDMS-MA comerciales fue un paso crucial para esta investigación, éste se logró utilizando la técnica de pre-polimerización. La separación del homopolímero y el macromonómero PDMS-MA no reaccionado fue realizada mediante la precipitación de estos en dietil éter/ metanol (1:1). Los estudios cinéticos de la homopolimerización se realizaron con la relación de la velocidad de propagación y terminación ($k_p/k_t^{1/2}$). Esta relación decrece al incrementarse el peso molecular de los macromonómeros. La velocidad aparente de propagación fue proporcional a $[I]^{2.2}$ y $[M]$ para condiciones de polimerización apropiadas. La temperatura máxima de polimerización fue calculada para los macromonómeros con $M_n = 1$ and 5 Kg/mol, siendo $T_c = 160^\circ\text{C}$ para $[M_1] = 0.88$ y $[M_5] = 0.11$ mol/L, para ambos homopolímeros.

Palabras clave: Macromonómero, poli(dimetil siloxano), polimerización de radicales libres, homopolimerización, purificación, pre-polimerización, cinética, temperatura máxima.

1. Introduction

Polyorganosiloxanes are industrially produced in large quantities for various purposes depending on molecular weight and composition. The Poly(dimethylsiloxane) (PDMS) is the most widely used inorganic polymer due its thermal stability, low flammability, low viscosity change vs. temperature, low surface tension, high compressibility, shear stability, dielectric stability and low toxicity. The highly viscous homopolymers have applications in the personal care arena, e.g. in cosmetics. They are

used in ink-paint and in the coating industry (Corey and Corey, 1998; Szycher, 1983; Koerner *et al.*, 1991). They can also be used as additives in lubricants for auto and oil industry. The inherent hydrophobic nature of siloxane coupled with ability to accumulate on the surface of polymers blends has allowed the poly(dimethylsiloxane) to be used widely to hydrophobize the surface of other materials, particularly in the case of polymers which by themselves lack of such properties (LeGrand and Gaines, 1970; Gaines, 1981; Azrak, 1974; Pennings and Bosman, 1980).

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PDMS-MA macromonomers can be synthesized by anionic polymerization, and free radical polymerization has so far been unable to produce homopolymers of polydimethylsiloxane. Only one patent has been reported by Gornowicz *et al.* (1998) for the homopolymerization of acrylate or methacrylate functionalized polydiorganosiloxane by means of emulsion polymerization as a method to obtain the homopolymer. They used different surfactants (ionic and anionic) and AIBN as the initiator. After 68 hours of reaction time, they obtained a product with high conversion of 82-wt%. The size exclusion chromatography (SEC) data in toluene and chloroform showed bimodal peak distributions i.e. the presence of un-reacted PDMS-MA.

Several kinetic aspects will need to be considered before homopolymerizing the macromonomer:

Their molecular weight being rather high ($10^3 < M < 10^4$), in most cases, the molar concentration of the polymerizable group that can be used in polymerization experiments is bound to be low ($\sim 1 \dots 0.1$ mmol/g macromonomer).

The intrinsic reactivity of the terminal reactive double bond (characterized by propagation rate constant k_p) may be smaller than that in a low molecular weight monomer exhibiting the same degree of instauration.

If the repeating unit of the macromonomer can be a target prone to transfer reactions, the probability for such side reactions to occur increases with the degree polymerization of the macromonomer (Tsukahara, 1993).

It could be expected that the rate of polymerization of macromonomers is reduced not only by the low concentration of the active sites in a macromonomer solution, but also to the lower accessibility of the growing radical end groups to the terminal unsaturated bonds further macromonomer molecules.

On the other hand, the bimolecular termination reaction is hindered by the sterical demands of the macromolecular units attached to the reactive sites.

For this propose the investigation of the homopolymerization behavior of PDMS-MA macromonomers by conventional free radical polymerization was evaluated. Polymerization of PDMS-MA macromonomer bearing methyl methacrylate end group was studied in homogeneous solution with respect to the following points: (i) characterization of commercial available macromonomers, (ii) optimization of homopolymerization conditions, (iii) separation of homopolymer from unreacted macromonomer, (iv) determination of molecular weight the dependence on the ratio $k_p/k_t^{1/2}$, measuring the ratio of polymerization with varying monomer and initiator concentrations, and (v)

thermodynamic studies, ceiling temperature estimation.

2. Experimental

2.1 Materials and methods:

The molecular weight of the poly(dimethylsiloxane) macromonomer was varied between $M_n=1, 5$ and 10 kg/mol (supplied by Chisso and Shin-Etsu). The macromonomers were purified by filtration over a two-layer column of silica gel (20 cm) and aluminum oxide (Al_2O_3) (20 cm) using absolute chloroform as the mobile phase. 2,2'-Azobisisobutyronitrile (AIBN, Aldrich) and 1,1'-azobiscyclohexane-1-carbonitrile (CAN, Aldrich) were re-crystallized from methanol, tert-butyl peroxide (TBP, Aldrich) was re-crystallized from chloroform and dimethyl 2,2'-azobisisobutyrate (V-601, Wako) was used as received. The solvents benzene and toluene were distilled over $LiAlH_4$, methanol and diethyl ether were used after distillation (using Mg and $LiAlH_4$ as drying agents respectively).

SEC chromatography: was performed in chloroform (for analysis grade) using refractive index (RI, Waters) as detector and a Waters-515 pump (flow rate = 1 mL/min) connected to μ -Styragel Waters columns ($10^6, 10^5, 10^4, 10^3$ Å nominal pore size). 20mg of the reaction mixture were dissolved in 1-mL of chloroform and filtered through 0.45- μ L Spartan filters to remove any gel fraction prior to injection.

To measure the conversion of poly(dimethylsiloxane) (PDMS-MA) macromonomers, the relationship between the polymer concentrations and their relative intensities in the SEC was studied. The refractive index (RI) of PDMS-MA ($n_D \approx 1.42$) is lower than that of chloroform ($n_D \approx 1.446$), hence the RI signal of the PDMS-MA macromonomer was negative in the chloroform-chromatogram. Since the refractive index of poly (PDMS-MA) ($n_D \approx 1.42$) is very close to that of chloroform, it appeared as a small positive signal in SEC traces. The monomer conversion was determined by calculating the decrease in the area of the SEC peaks of the macromonomer throughout the polymerization.

1H -NMR measurements were performed with a Bruker 400 MHz spectrometer, in $CDCl_3$ as the solvent. A concentration of compound 20-30 mg/mL was applied.

Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) analysis: The sample was analyzed using a Bruker-Franzen REFLEX III (1998) spectrometer equipped with a nitrogen laser (337 nm), tetrahydrofuran (THF) as the solvent and 2,5-dihydroxy-benzoic acid (DHB) as the matrix. DHB was dissolved in 5- μ L

THF and the ratio mixing between matrix and analyte was 3:1 wt%.

3. Reactions without Pre-polymerization

All polymerizations were carried out in a 20-mL glass bottle with PTFE septa coated screw caps. The initiator was weighed into the bottle followed by the macromonomer and solvent at the desired ratios (Table 1). The solutions were freeze-thawing cycles three times. The solutions were allowed to stir at the desired temperature. The poly(dimethylsiloxane) was removed by precipitation in methanol or a mixture of methanol/diethyl ether (1:1) for three times. The product was dried under vacuum overnight at room temperature.

Table 1. Homopolymerization conditions of poly(dimethylsiloxane) $M_n = 5000$ g/mol from Shin-Etsu, the macromonomer was used without pre-polymerization. ($T = 60^\circ\text{C}$, benzene and 4.78 mol% V-601).

Id	Reaction time (hours)	Macromonomer Concentration (mol/L)
A1	72	0.098
A1	48	0.098
A1	24	0.098
A1	10	0.098
A1	4	0.098
A2	120	0.057
A2	72	0.057
A2	48	0.057
A2	24	0.057
A3	72	0.044
A3	24	0.044
A3	10	0.044

3.1 Pre-polymerization procedure

Macromonomer $M_n = 5,000$ g/mol: 1-mmol (5-grams) of poly(dimethylsiloxane) with a methyl methacrylate end group was weighed into a 100-mL two-necked flask, 0.04-mmol (9.2-mg) of initiator (V-601) was added and dissolved in 12.5-mL of dried benzene. The flask was sealed with a rubber septum, purged with nitrogen and heated to 60°C after three freeze-thawing cycles (Table 2). The polymerization of the macromonomer was carried out during 24 hours of reaction time. Then any solvent excess was removed under vacuum at -70°C . A 100-mL separation funnel was charged with a mixture of homopolymer-remnant macromonomer, and a mixture of methanol/diethyl ether (1:1) was added to the funnel. After the solution was shaken, it separated into two phases. The light phase contained the unreacted macromonomer dissolved into the solvent mixture. The unreacted macromonomer was recuperated by slow evaporating the solvent mixture at room temperature. The macromonomer was

purified by filtration over a two-layer column of silica gel (20-cm) and aluminum oxide (Al_2O_3) (20-cm) using absolute chloroform as the mobile phase. The solvent was removed on a rotary evaporator and the macromonomer was dried under vacuum at room temperature overnight. 3.89 g of clear, colorless liquid was obtained. SEC chromatography was measured to verify the purity of the macromonomer.

Table 2. Purification conditions of PDMS-MA macromonomer (MM).

M_n of MM (g/mol)	m_{MM} (g)	n_{MM} (mmol)	V_{benzene} (mL)	m_{V601} (mg)	Reaction time (hours)	Yield (g, wt%)
1000	10	10	25	46.04	12	7.90, (79)
5000	5	1	12.5	9.20	4	3.89, (78)
10000	10	1	5	9.30	13	8.50, (85)

3.2 Rate of polymerization experiments (R_p).

Homopolymers of PDMS-MA macromonomers were prepared by free radical polymerization in bulk. In a typical experiment, PDMS-MA macromonomer and V-601 in dried benzene was placed in a 100-mL round-bottomed flask. The flask was sealed with a rubber septum, purged with nitrogen, and heated to 60°C after three freeze-thawing cycles. The unreacted macromonomer was removed by three times precipitation in methanol or a mixture of methanol/diethyl-ether (1:1). The product was dried under vacuum overnight at different temperatures. The reaction mixture compositions for the rate of polymerization experiments are summarized in Tabel 3.

Table 3. Homopolymerization conditions for estimation of R_p (Reaction temperature= 60°C)

Id	Macromonomer M_n (Kg/mol)	V_{benzene} (mL)	MM (g)	V-601 (mg)	Reaction time (hours)
H1	1	5.0	5	23.2	10
H5	5	12.5	5	4.6	10
H10	10	25.0	5	4.9	10

3.3 Ceiling temperature experiments.

The macromonomers were used after pre-polymerization. Polymerizations were carried out in sealed bottles, using xylene as solvent, 2-mol% of initiator. Four different initiators were used depending on the reaction temperature: a) 2,2'-Azobisisobutyronitrile (AIBN) or dimethyl 2,2'-Azobisisobutyronitrile (V-601) in the range $60-700^\circ\text{C}$, b) 1,1'-azobiscyclohexane-1-carbonitrile (CAN) in the range $80-1000^\circ\text{C}$ and c) tert-butyl peroxide (TBP) in the range $110-1300^\circ\text{C}$ (Table 4).

Table 4. Homopolymerization conditions for estimation of T_c .

Id	Macromonomer M_n (Kg/mol)	V_{xylene} (mL)	MM (g)	V-601 (mg)
H1	1	0.70	10	46.4
H5	5	0.15	10	9.2

4. Results and Discussion.

4.1 Kinetic.

According to Frye *et al.* (1970) the polymerizations of macromonomers showed obey the standard kinetic laws of free radical polymerization.

The steady-state concentration of all growing chains is given by:

$$\sum[M_i \cdot] = \left(\frac{k_i [I]}{k_t} \right)^{1/2} \quad (1)$$

$[M_i \cdot]$: concentration of radical monomer i , k_i : initiation constant, k_t : termination constant and $[I]$: initiator concentration.

This means that $\sum [M_i \cdot]$, which is somewhat difficult to evaluate experimentally, does not have to be measured for a particular reaction. In Eq. (1) it is expressed in terms of parameters which are either known or can be readily determined.

A small amount of monomer disappears with the formation of active centres but most of the molecules are consumed during the propagation reaction for which the kinetic equation is

$$\frac{-d[M]}{dt} = k_p [M] \sum[M_i \cdot] \quad (2)$$

The steady-state concentration of active centres is given by

$$\frac{-d[M]}{dt} = k_p [M] \left(\frac{k_i [I]}{k_t} \right)^{1/2} \quad (3)$$

$$\text{Or,} \quad \frac{-d[M]}{dt} = \frac{k_p k_i^{1/2}}{k_t^{1/2}} [M] [I]^{1/2} \quad (4)$$

The rate of consumption of a monomer with time is usually called the rate of polymerisation and is given by Eq. (4), which applies only under steady-state conditions. With low molecular weight monomers often the rate of polymerisation is fast and only a small proportion of initiator breaks down into radicals until full conversion of the monomer. This means that $[I]$ is effectively constant throughout the reaction and Eq. (4) can be written as:

$$\frac{-d[M]}{dt} = K_{eff} [M] \Rightarrow \quad (5)$$

$$\ln \left(\frac{[M]}{[M]_0} \right) = -K_{eff} t \quad (6)$$

This demonstrates a simple pseudo-first-order dependence in $[M]$. In this case K_{eff} is an apparent composite rate constant.

With macromonomers, the kinetic is affected by the fact that the reaction times can exceed the half-life time of the initiator by four. Hence, $[I]$ is not constant for large reaction times, and Eq. (6) is modified in Eq. (7), by taking into account the time dependence of the initiator concentration

$$\frac{d[M]}{dt} = K'_{eff} [M] \sqrt{[I]} \quad (7)$$

where: $[I] = [I]_0 e^{-k_d t}$, one obtains

$$\ln \frac{[M]}{[M]_0} = -\frac{2K'_{eff}}{k_d} \sqrt{[I]_0} \left(e^{\frac{k_d t}{2}} - 1 \right) \quad (8)$$

For small reaction times ($t \ll k_d/2$), the exponential $e^{\frac{k_d t}{2}}$ can be replaced by $1 - (k_d/2)t$, and again a first-order law is obtained Eq. (9)

$$\ln \frac{[M]}{[M]_0} = -K'_{eff} \sqrt{[I]_0} t \quad (9)$$

For large reaction times, the exponential term vanishes (Eq. (10)), and Eq. (8) transforms into Eq. (11).

$$\lim_{t \rightarrow \infty} e^{\frac{k_d t}{2}} \rightarrow 0 \quad (10)$$

$$\lim_{t \rightarrow \infty} \ln \frac{[M]}{[M]_0} = \frac{2K'_{eff}}{k_d} \sqrt{[I]_0} \quad (11)$$

Eq. (11) states that after complete consumption of the initiator, a finite monomer conversion will be obtained that is proportional to the square root of the initial initiator concentration.

4.2 Chemical characterization of the PDMS-MA macromonomer.

Complete functionalization a polymer chain with a polymerizable unit is of course, the most desirable situation to create a macromonomer. This means either relying on clean reactions that install the desired groups qualitatively or a need to purify the products. In general, purification procedures are not feasible, since the physical properties of the macromonomer are most often entirely controlled by the nature of the long polymeric backbone and not by the terminal group. Purification is mainly useful to separate low molecular weight reagents from the high molecular weight macromonomer. Quantitative reactions are, of course, the objective, however it should be noted that the reactions on polymers often do not proceed as readily as those on molecular weight substrates. Moreover, in order to optimize the chances of the complete incorporation of functionality and to have a well-defined macromonomer, it is often desirable to have as few steps as possible in this preparation.

If the macromonomer is sufficiently reactive, copolymerization or polymerization to complete conversion and analysis of unpurified reaction mixture by SEC often provide compelling evidence for the presence of at least one polymerizable end group per polymer chain. In this case, the only limitation is the sensitivity of the SEC system.

Fig. 1 shows the synthesis of PDMS-MA macromonomers. It is common knowledge that during the ring opening polymerization of cyclotrisiloxane (D₃), a side reaction appears to break the cycle. Hence, the resulting PDMS-MA are not exclusively compounds of $(-\text{OSi}(\text{CH}_3)_2-)_n$ species, but may also contain considerable amounts of $(-$

$\text{OSi}(\text{CH}_3)_2\text{--})_{3m+1}$ and $(\text{--OSi}(\text{CH}_3)_2\text{--})_{3m+2}$ polymers (Frye *et al.*, 1970).

At larger monomer conversions, further “scrambling” reactions cause the formation of: i) non-functionalized and ii) bifunctional macromolecules. In high conversions, polymerization experiments the latter can cause gelation.

The NMR technique offers a good method to determine nature and concentration of the end-group of the macromonomer, but it cannot distinguish between mono- and polyfunctional polymer chain. Fig. 2 shows the NMR spectra of PDMS-MA macromonomer before purification. Characteristic peaks of poly(dimethylsiloxane) with a methyl methacrylate end group were observed. The protons of $=\text{CH}_2$ end group are assigned a signal at $\delta = 5.5$ and 6.0 ppm (Fig. 2). Further absorptions at $\delta = 0$ ($-\text{CH}_3$ proton of $-\text{Si}(\text{CH}_3)_3$) and $\delta = 0.8$ (CH_2 proton of $-\text{CH}_2\text{--Si}(\text{O--CH}_3)_2$). The ^1H -NMR signals at $\delta = 3.8$ ppm could not be assigned (i).

The signal at $\delta = 3.8$ ppm (signal i, in Fig. 2) is due to an impurity that is contained within the macromonomer. This impurity could be removed by filtration of the macromonomer first through a silica oxide column and subsequently on aluminium oxide column, using chloroform as the solvent. The ^1H -NMR spectrum of the monomer after purification (Fig. 3) demonstrated that the impurity could be removed by simple filtration. The impurity can be unreacted Si-H groups; this technique shows that only mono-functional macromonomers were found (Frye *et al.*, 1970).

MALDI-TOF MS of the PDMS-MA macromonomer was performed to correlate the ^1H -NMR and determine the end-group in the sample.

Fig. 4 depicts the MALDI-TOF spectra of PDMS-MA from Shin-Etsu (2a). The products exhibit three sub distribution arising from the different molecular species previously mentioned ($(\text{--OSi}(\text{CH}_3)_2\text{--})_{3m}$, $(\text{--OSi}(\text{CH}_3)_2\text{--})_{3m+1}$, and $(\text{--OSi}(\text{CH}_3)_2\text{--})_{3m+2}$).

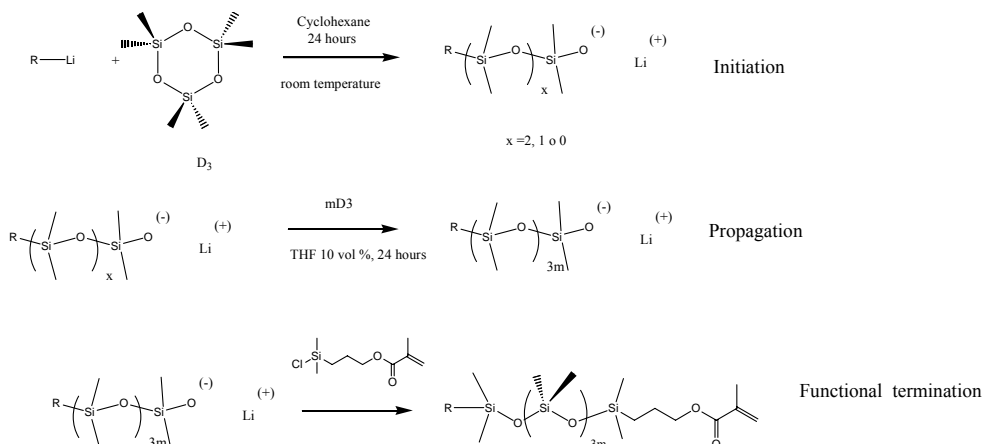


Fig. 1. Synthesis of PDMS-MA macromonomer.

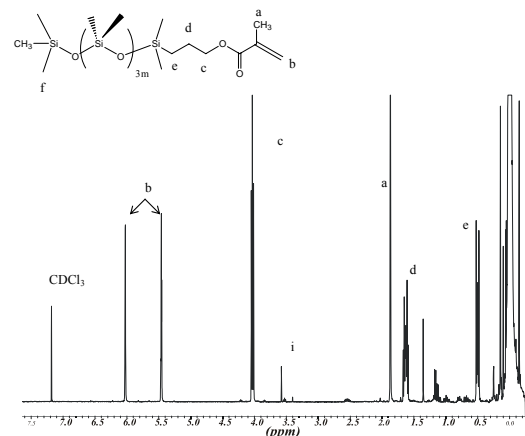


Fig. 2. ^1H -NMR spectra of PDMS-MA monomer from Shin-Etsu before purification.

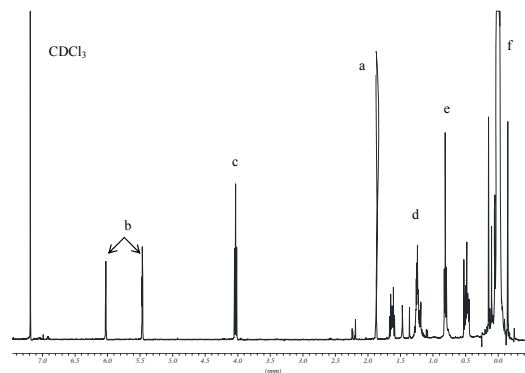


Fig. 3. ^1H -NMR of PDMS-MA monomer after purification.

According to Fig. 4, three end-group possibilities were found. The Bi-functionality methyl methacrylate end-group occurred in 8-wt%.

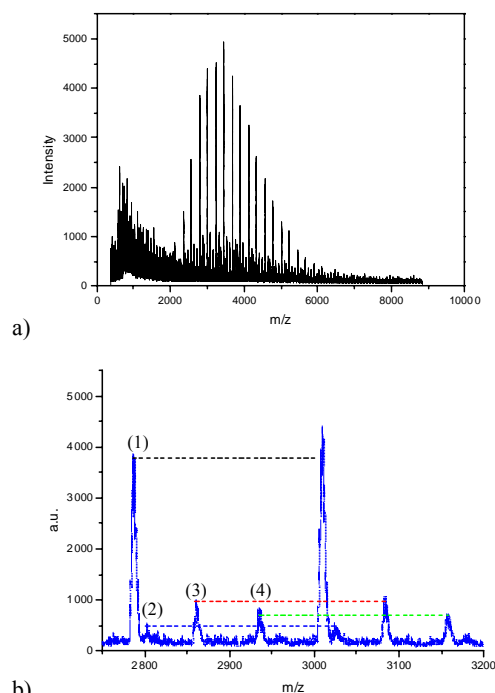


Fig. 4. (a)MALDI-TOF spectra of the PDMS-MA macromonomer from Shin Etsu, and (b)Expanded region of spectra of (a).

4.3 Polymerization conditions

Some time/conversion of curves the technical macromonomer are plotted in Fig. 5. From the sigmoidal curves shown at high macromonomer conversion, “inhibition period” of 24 to 30-hours arose. Although the accessibility of the growing radicals to the unsaturation of the macromonomer is much lower than with small monomers in the same polymerization conditions (i.e. methyl methacrylate), the occurrence of long induction periods must be attributed to the presence of impurities.

From these preliminary data, some dues for the correct handling of the PDMS-macromonomer with respect to radical polymerization were obtained:

The presence and quantity of solvent influences the polymerization in several ways: i) at lower-monomer concentrations the viscosity of the reaction medium is lowered and the diffusion of macromolecules is enhanced, especially at high conversion; solvents can also prevent gel effects; ii) if the solvent solvates the backbone chain as well as the macromonomer, it acts as a compatibilizer and facilitates their mutual interpenetration; and iii) conversely, if the solvent is better for one type of polymer than for the other, preferential solvation effects are induced (Tsukahara, 1993; Percec 1988).

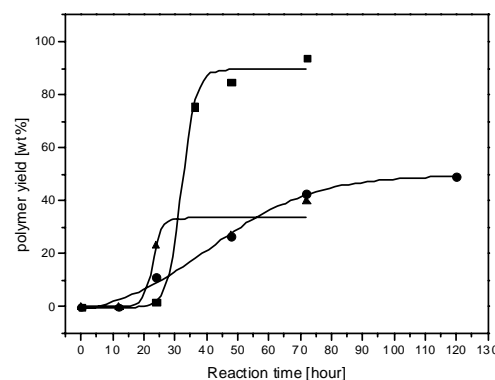


Fig. 5. Homopolymerisation conversion at different PDMS-MA macromonomer concentration: ■ 0.098, • 0.057 and ▲ 0.044 mol/L. Polymerization conditions: $[I] = 4.78$ mol%, in benzene at 60°C , macromonomer used without the pre-polymerization procedure.

Bifunctional poly(dimethylsiloxane) macromonomer is present in the raw material. The chemical characterization of the poly(dimethylsiloxane) demonstrated the present of bifunctional poly-(dimethylsiloxane) molecule, and the homopolymerization reaction of such a material is expected the causes serious problems, like gel formation during the reaction.

Two optimal conditions to homopolymerize the untreated PDMS-MA macromonomer ($M_w = 5,000$ g/mol, from Shin-Etsu) were found: $[M] = 0.098$ mol/L, $[I] = 4.8$ -mol% for 12 hours at 60°C and $[M] = 0.098$ mol/L, $[I] = 8.8$ -mol% for 12 hours at 60°C .

4.4 Separation of the unreacted macromonomer and homopolymer

Since poly(macromonomer) and unreacted monomer was attempted no complete conversion was achieved with technical PDMS-MA the separation of the remaining unreacted macromonomer can be removed by two different methods: 1) Preparative GPC (Gel Permeation Chromatography) and 2) by precipitation in solvents. The first method was declined, as only a small amount of polymer can be using this technique. In contrast, the second method offers the real possibility of removing the remnant macromonomer. This method can be accomplished by SEC chromatography. It is also worthwhile examining the mother liquors from precipitation techniques to determine whether the separation of the polymer has been complete.

The solubility of the mixtures of homopolymer and macromonomer were studied in common solvents (Table 5) (Ivin, 1973). Unfortunately, the macromonomer and homopolymer present the same solubility. Different

mixtures of solvent/non-solvent pairs were prepared to dissolve the macromonomer and precipitate the polymer (Table 6). Table 6 shows the results of the solubility of the homopolymer in a mixture of solvents. The unreacted macromonomer was removed by precipitation three or four times in a mixture of methanol/diethyl-ether 1:1. Then the polymer was dried under vacuum overnight at room temperature.

Table 5. Solvents and non-solvents for poly(PDMS-MA)

Solvent	Non-solvent
Hydrocarbons, benzene, toluene, chloroform, xylene, diethyl ether, methyl ethyl ketone (above 13 °C), ethyl acetate, acetone (hot).	Lower alcohols (methanol, ethanol, and isopropanol), water, acetone cold, dioxane, moderately concentrated acid and alkalis, ethylenglycol.

1-wt% homopolymer in solvent at room temperature.

Table 6. Solubility test of PDMS-MA homopolymers in different solvent mixtures. (At room temperature).

Solvent 1	Solvent 2	Mixture	Solubility of polymer
Methanol	Petrolether	1 : 3	Sol.
		1 : 1	Sol.
		3 : 1	Sol.
Methanol	Ethyl methyl ketone	1 : 3	Sol.
		1 : 1	Sol.
		3 : 1	Sol.
Methanol	Diethyl ether	1 : 3	Sol.
		1 : 1	Insol.
		3 : 1	Sol.

Sol.: Soluble, Insol.: Insoluble.

The product was characterized by SEC chromatography to prove that the unreacted macromonomer was removed. SEC diagrams of the product before and after precipitation are shown in Fig. 6. The products contained only 3-wt% of unreacted macromonomer.

Liquid viscous products soluble in aromatic and hydrocarbon solvents and non-soluble in lower alcohols and moderately concentrated alkalis and acid (Table 5) were obtained.

4.5 Synthesis of Poly(PDMS-MA) after pre-polymerization

The precipitation method described above offers an efficient technique to eliminate impurities by means of the "pre-polymerization technique". The macromonomer was polymerized to low conversion ($p < 20\%$) and separated from the polymer. During the reaction, all inhibiting

impurities become destroyed and the recuperated macromonomer is of high purity grade. Furthermore, the content of bifunctional molecule becomes reduced, since their reaction probability is twice as large with monofunctional macromonomers.

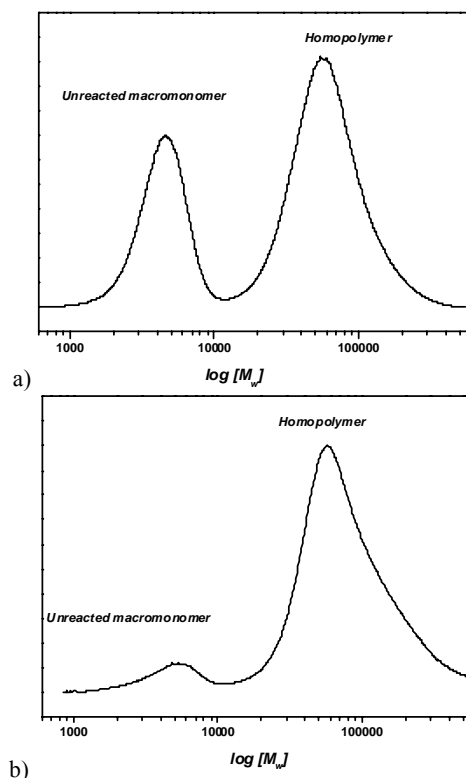


Fig. 6. SEC chromatograms of homopolymer #A40 in CHCl_3 . (a) before and (b) after three precipitations in methanol/diethyl-ether 1:1. Polymerization conditions: $[M]=0.098$ mol/L, 4.78 mol% V-601 at 60°C for 24 hours using benzene as the solvent medium, the macromonomer was used without the pre-polymerization procedure.

The time/conversion curves obtained with PDMS-MA, purified by the pre-polymerization method, are depicted in Fig. 7. The induction periods were completely eliminated and it was possible to achieve high conversion of the macromonomers ($p > 95\%$) without gelation of the reaction mixture. The presented data allowed for kinetic analysis of the homopolymerization of PDMS-MA in Table 7 were calculated using Eq. (7). Both values of the apparent rate of homopolymerisation and the composite constant k_{eff} (Eq. (8)) depended on the macromonomers molecular weight.

As the degree of conversion increased the R_p decreases monotonically as the polymerisation proceeded. This behaviour of the time/conversion curves is common in the radical polymerisation of monomers (independent of $[M]$ and M_w) (Tsukahara,

1993). The dependence of R_p on the macromonomer concentration was first order and one-half order on $[I]$ (Eq. (4)). It is seen from Fig. 8 and Table 7 that R_p increased substantially with decreasing M_w of the macromonomer; as to be expected from the enhanced sterical hindrances caused by larger macromolecular coils. This is quantified with Fig. 9 depicting the ratio $k_p/k_t^{1/2}$ to become lower with larger molecular weight of the macromonomer. It seems that $k_p/k_t^{1/2}$ follows a simple scaling law in the region between 100 g/mol (= MMA) and approximately 5000 g/mol ($k_p/k_t^{1/2} \sim 10^{-7} \cdot M^{3/2}$).

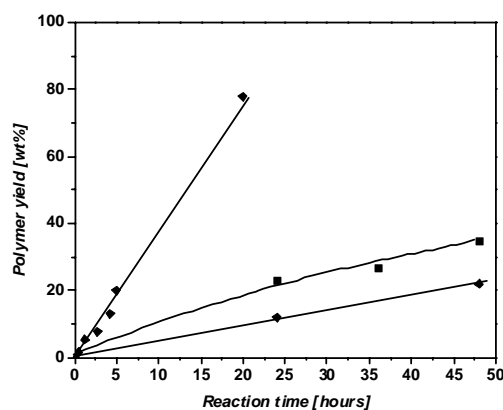


Fig. 7. Effect of improved macromonomer impurity: ◆ Pre-polymerization and chromatography column, ■ chromatography column and ▲ without pre-polymerization method. Polymerization conditions: $[M] = 0.044$ -mol/L, $[I] = 4.8$ mol%, in benzene at 60°C.

The increase in the viscosity of the polymerization media influences the efficiency of the initiator f and it becomes less effective at high $[M]$ due to the mobility of the primary radical (cage effect) (Odián, 1993). The slope of straight line fitted data on $\log R_p$ against $\log [M]$ is 2.2 in . This value indicated the reduction in the mobility of the growing radicals during the polymerization.

Table 7 resumes the chemical characterization of homopolymer obtained after pre-polymerization method. Degree of polymerization ($\langle X_n \rangle$) was

calculated from number molecular (M_n), the homopolymers presents narrow polydispersity between 1.2 to 1.9.

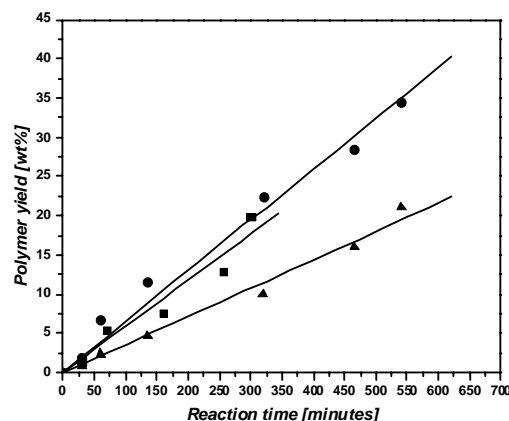


Fig. 8. Kinetic plots of homopolymerization of PDMS-MA macromonomer: ■ $M_n=5,000$ g/mol, from Shin-Etsu, ● $M_n=1,000$ and ▲ $M_n=10,000$ g/mol from Chisso after second reaction. Polymerisation conditions: $[M] = 0.049$ mol/L, $[V-601] = 2$ -mol% in benzene at 60°C.

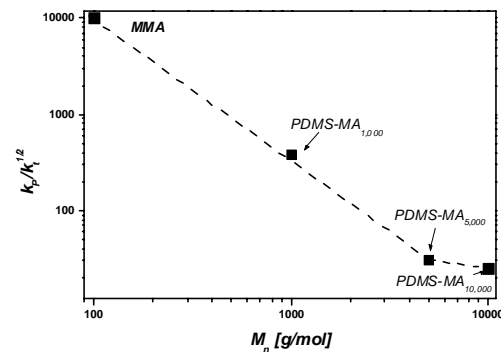


Fig. 9. Plots of $k_p/k_t^{1/2}$ versus M_n . Polymerization conditions: $[I]_0 = 2$ -mol%, PDMS-MA at 60°C.

Table 7. Results data of homopolymerization of PDMS-MA, $M_n = 1,000$ g/mol, 5,000 and 10,000 (from Chisso and Aldrich), macromonomer used after pre-polymerization procedure.

Id	Macromonomer M_n (Kg/mol)	$[M]$ (mol/L)	$[I]$ (mol/L)	Yield wt%	$M_n^{(a)}$ (Kg/mol)	$M_w^{(a)}$ (Kg/mol)	$PDI^{(a)}$	$\langle X_n \rangle$	R_p (mol/L-h)	K_{eff} (min ⁻¹)	$k_p/k_t^{1/2}$
H1	1	0.492	0.0098	90	35	50	1.5	35	1.92 ± 0.24	$0.00006490 \pm 4 \times 10^{-8}$	387.40
H5	5	0.056	0.0011	92	27	33	1.2	5	$0.0389 \pm 4.2 \times 10^{-4}$	$0.0000116 \pm 3 \times 10^{-7}$	31.03
H10	1	0.016	0.0003	94	120	228	1.9	12	$5.77 \times 10^{-6} \pm 5.8 \times 10^{-8}$	$0.00000036 \pm 7 \times 10^{-8}$	25.68

(a) SEC molecular weight of poly(PDMS-MA), PDI= polydispersity index

(b) R_p = polymerization rate

(c) K_{eff} = apparent composite rate constant

4.6 The equilibrium between PDMS-MA macromonomer and its polymer

In any exothermic chain polymerization reaction there is, at a given concentration of monomer, a temperature (known as the ceiling temperature) above which polymerization does not occur. Conversely, at any temperature, there is a certain equilibrium monomer concentration, which is independent of the amount of polymer in the system if the chain length is sufficiently large. A study of this equilibrium as a function of the temperature provides a method for the determination of the heat and entropy of polymerization.

The kinetics at the ceiling temperature where the rates of polymerization and depolymerization are equal leads to Eq. (12) (Dainton and Ivin, 1958)

$$k_p [M_x^*] [M] = k_d [M_{x+1}^*] \quad (12)$$

k_p = Propagation constant, k_d = De-propagation constant, M_x^* = Concentration of activated chain and M_{x+1}^* = Concentration of activated chain in equilibrium.

In Eq. (12) the quantities in brackets represent the concentrations. Activated chain end are denoted as M_x^* and M_{x+1}^* is the concentration of the activated chain in equilibrium, and k_p and k_d are the propagation and de-propagation constants.

Polymerization of methacrylic esters by radical mechanism has been studied extensively. As seen, the ceiling temperature depends on monomer concentration, and the steric effect of the group attached to the reactive double bond. It is the general tendency of T_c to decrease with reduced monomer

concentration, and with enlarged steric demand of the side units of the monomer (Table 8).

The ceiling temperature of PDMS-MA macromonomer was estimated by measuring the degree of polymerisation $\langle X_n \rangle$ at several temperatures below T_c , and extrapolation of the line to a degree of polymerization of one (Eq. (13)). This method has the advantage that the chain length may remain quite high even to within a few degrees of the ceiling temperature. The extrapolated value for T_c then corresponds to the limiting value for long chains. The limiting slope $(dX_n/dT)_{T_c}$ is proportional to the chain centers and the heating of polymerization (Dainton and Ivin, 1958; Ivin, 1973)

$$\ln X_n = \Delta H - \frac{\Delta S}{T} \quad (13)$$

ΔH = Heat change for the polymerization process, ΔS = Entropy change for the polymerization process and X_n = Degree of polymerization.

Formation of very short chain polymers is to be expected in the vicinity of T_c because of the variation of ΔG_x . Again, we have a physical analogy in the effect of crystal size on melting point; this effect is only detectable when the surface free energy contributes appreciably to the molar free energy of the solid, i.e. for extremely small crystals.

The equilibrium monomer concentrations ($[M_e]$) were obtained according Eqs. (14) and (15) (Table 9)

$$\ln [M_e] = \frac{\Delta H}{RT_c} + \frac{\Delta S}{R} \quad (14)$$

$$T_c = \frac{\Delta H}{\Delta S} \quad (15)$$

Table 8. Published ceiling temperature of methacrylic esters monomers.

Monomer	[M] mol/L	T_c (°C)	Reference
Methyl methacrylate	Pure monomer	220	Small (1953)
Methyl methacrylate	1.000	160	Otsu <i>et al.</i> (2003)
Methyl methacrylate	0.820	155	Otsu <i>et al.</i> (1980)
Methyl methacrylate	0.611	135	Otsu <i>et al.</i> (1996)
Methyl methacrylate	0.640	>140	Otsu <i>et al.</i> (2003)
Methyl methacrylate	0.515	140	Otsu <i>et al.</i> (1996)
o-Phenyl methacrylate	0.640	>140	Otsu <i>et al.</i> (1996)
o-methylphenyl methacrylate	0.640	140	Otsu <i>et al.</i> (1996)
2,6-Dimethylphenyl methacrylate	0.640	77	Otsu <i>et al.</i> (1996)
2,6-Di-terbutylphenyl methacrylate	0.640	81	Otsu <i>et al.</i> (1996)
N-Phenyl methacrylamide	0.611	125	Otsu <i>et al.</i> (1980)
N-n-Butyl methacrylamide	0.611	122	Otsu <i>et al.</i> (1980)

Table 9. Ceiling temperatures for the PDMS-MA macromonomers.

M_w (g/mol)	[M] (mol/L)	T_c (°C)	$[M_e]$ (mol/L)	T_{d10} (°C)	ΔH_x (KJ/mol)	ΔS_x (KJ/mol-K)	ΔH_m^0 (1) (KJ/mol)
MMA (a)	0.82	155	-	330 ⁽¹⁾	56.12	117.26	58.21
1,000	0.884	170 ± 0.076	0.082	350	-46.95 ± 0.30	-20.77 ± 0.35	-50.25 ± 0.80
5,000	0.112	169 ± 0.087	0.52	383	-11.39 ± 0.50	-5.40 ± 0.24	-12.02 ± 0.38

ΔH_x and ΔS_x calculated from Eq. (12).

ΔH_m : calculated from calorimetric method(DSC measures).

T_{d10} = Decomposition temperature from TGA experiments. (a): Value from literature.

Fig. 10 shows the plots of $\log X_n$ against $1/T$, to determine T_c by extrapolation of measured values to degree of polymerization to one. Estimated T_c 's are summarized in Table 9. T_c of macromonomer was not seemingly dependent on the molecular weight. The value estimated for the poly(dimethylsiloxane) macromonomer is similar to the methyl methacrylate monomer at the same monomer concentration. As seen in Table 9, the ceiling temperature is below the decomposition temperature or thermal stability (T_{d10}). The enthalpy and entropy of polymerization in equilibrium were calculated from Eq. (14) and in Table 9 there is good agreement with the calorimetric heats (PDMS₅₀₀₀-MA: $\Delta H_x = -2.7 \pm 0.5$, $\Delta H_{DSC} = -2.9 \pm 0.4$). Small discrepancies are already accountable as variations of ΔH with the temperature (ΔC_p is commonly of the order -0.418 KJ/mol-deg. for the polymerization).

Conclusion

Commercial available PDMS-MA macromonomers must be intensively purified prior to use by means of pre-polymerisation. The homopolymer of PDMS-MA macromonomer could be synthesised by free radical polymerization. Ceiling temperatures were estimated for two macromonomers ($M_n = 1$ and 5 Kg/mol) to be $T_c = 160^\circ\text{C}$ ($[M_i] = 0.88$ and $[M_s] = 0.11$ mol/L), for both homopolymers. Both parameters indicate that the radical polymerisation kinetics and thermodynamic behaviours of PMDS-MA are not different from conventional small methyl methacrylates monomers, except that the monomer concentration is lower.

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