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Macroporous Gels. 4. An NMR Study of the Formation of Macroporous Gels Containing Trimethylolpropane Trimethacrylate

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ABSTRACT: The radical polymerization of trimethylolpropane trimethacrylate (TRIM) and the radical copolymerization of TRIM and methyl methacrylate (MMA) in solution were studied by ^{1}H NMR in situ measurements. The conversion at the point of gelation was determined. A method based on line-width measurements of an inert component in the system is suggested for the estimation of the gel point of the system. An investigation of the influence of the polymerization time and temperature on the amount of unreacted methacrylate groups has also been performed. The number of unreacted double bonds decreased with increasing polymerization time and temperature even after 100% monomer conversion. From this investigation it was possible to divide the polymerization of TRIM into three discernible steps.

Introduction

Polymerization of trimethylolpropane trimethacrylate (TRIM) in a solvent results in a macroporous gel.[1,2] When toluene was used as pore-forming agent, the resulting macroporous gel had two pore size distributions, one consisting of small pores (radius < 50 Å) and one of large pores (radius > 50 Å).[1] The pore size distribution of small pores was very narrow and probably caused by the structure of the monomer.[1] Different pore size distributions were obtained by changing the solvent and/or by copolymerization of TRIM with a suitable comonomer.[2,3]

In this paper we present an ^{1}H NMR study of the course of polymerization for both the TRIM and the TRIM–methyl methacrylate (MMA) systems in two different solvents (ethyl acetate and toluene) as well as the level of conversion at which the gel formation occurs in the former system.

The progress of the polymerization process can be followed by analyses of the monomer consumption in the system. One way to do this to interupt the polymerization at different stages and analyze the unreacted monomer–solvent mixture. Due to the effect of gel formation this method can be difficult to perform. Another way is to use an FT-NMR spectrometer and make the polymerization in situ while collecting spectra.

Highly cross-linked polymers can be analyzed by IR spectroscopy[4] or by solid-state ^{13}C FT-NMR (CP-MAS-DD).[1] The latter method was used to determine the residual amount of unreacted carbon–carbon double bonds as a function of time and temperature.

Experimental Section

Polymerization (NMR Kinetics). The mixture of trimethylolpropane trimethacrylate (TRIM, technical quality containing more than 98% TRIM from Merck AG or Alfa Products), a solvent (toluene or ethyl acetate, analytical grade), and in copolymerizations methyl methacrylate (MMA, analytical grade) was transferred into a 50-mL hypo-vial containing 0.1% (w/w) AIBN (analytical grade). The mixture used consisted of 30% monomer and 70% solvent. In the copolymerization experiments the monomer was a mixture of 20% (v/v) MMA and 80% TRIM. Nitrogen gas was bubbled through the solution for at least 1 min before the vial was sealed. A sufficient amount for analysis was then transferred into an NMR sample tube and 1–2 droplets of C_6D_6 were added.

Polymerization (Double-Bond Consumption). A polymerization experiment was performed as follows. AIBN, 20 mg, was weighed into a 50-mL hypo-vial. The vial was sealed, evacuated, and filled with nitrogen. Then 20 mL of a solution containing monomer (TRIM 30%) and solvent (toluene 70%) was added. The vial was placed in a shaking bath at elevated temperature (73 °C) and was kept there for the specified time. The resulting polymers were ground and dried at 60 °C in vacuum for at least 24 h before the determination of unreacted double bonds was made.

Kinetic Measurements with NMR. The in situ ^{1}H NMR experiments were carried out at different temperatures with a Varian XL-200 spectrometer operating at 200 MHz. The pulse angle used was 81° and the waiting time between the pulses was at least $3T_1$. T_1 measurements were performed for all hydrogen atoms in the TRIM monomer according to the inversion–recovery sequence with delay times longer than $5T_1$ of the slowest relaxing hydrogen. All chemical shifts are reported in parts per million downfield from TMS. An NMR spectrum was recorded before heating was commenced and the others at the reaction temperature. The interval between the spectra was 1 s and the time for one spectrum to be collected was 73 s.

Determinations of Unreacted Carbon–Carbon Double Bonds. The amount of unreacted carbon–carbon double bonds was determined by high-resolution solid-state ^{13}C NMR spectroscopy using cross-polarization (CP), magic-angle spinning (MAS), and high-power decoupling (DD) (Varian XL-200 with solid sample accessories). Carbonyl groups conjugated with a double bond have a lower chemical shift (166 ppm versus TMS) than the unconjugated, reacted, ones (176 ppm versus TMS). The difference was large enough to almost completely resolve the two peaks. This together with nearly similar contact times makes quantitative measurements possible.[1]

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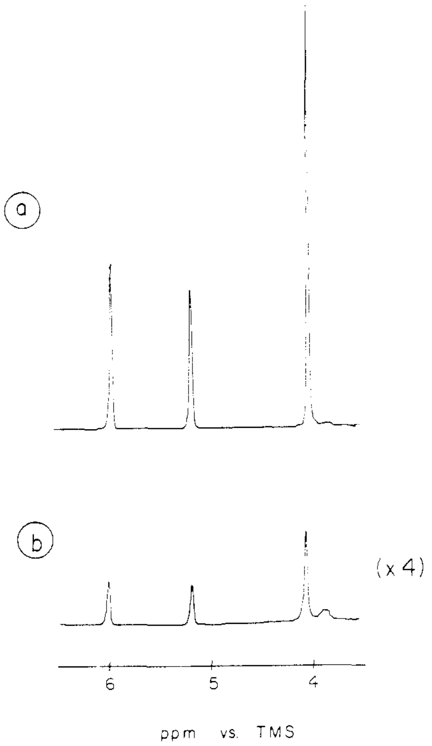

Figure 1. ^1H NMR spectrum from in situ polymerization of TRIM in the presence of toluene at 80 °C. The peaks between 5 and 6 ppm represent the $H_2C=$ part of the methacrylate group and the peak at 4 ppm represents the protons in the CH_2 groups that is placed between the oxygen and the tertiary carbon. (a) Spectrum at 0% conversion; (b) spectrum at 90% conversion (magnification level = 4×).

Results and Discussion

The formation of poly(TRIM) was investigated by polymerization in situ in the NMR apparatus. This makes it possible to follow the conversion by determination of the amount of unreacted TRIM molecules in the bulk. Figure 1 shows two ^1H NMR spectra of the TRIM–toluene system (3.5–6.5 ppm). The spectrum in Figure 1a is from the start of the polymerization while the second one, shown in Figure 1b, is from a conversion degree of about 90% (the magnification level in Figure 1b is 4×).

Single chains at the beginning of the polymerization could affect the NMR spectra. However, no such effects were observed. We have therefore assumed that the methacrylate groups were not visible when incorporated into the polymer. This was supported by the fact that a ^1H NMR spectrum of poly(TRIM), without monomer, in a solvent does not show any signals at all from the polymer. The areas of the peaks in the spectrum would then represent almost the total amount of monomer molecules.

A 100% conversion of the TRIM molecules means that at least $^1/_3$ of the methacrylic groups have reacted. It is, however, probable that the amount of reacted methacrylate groups exceeded 75% according to measurements with ^{13}C solid-state NMR which show that less than 17% remain unreacted after 2 h of polymerization (Table III).

A similar behavior was also observed when TRIM and MMA were copolymerized into macroporous copolymers. Since MMA has a peak at 3.5 ppm, it was possible to follow the consumption of TRIM and MMA monomers independent of each other.

Kinetics of Homopolymerization. In Figure 2 the conversion is plotted against the polymerization time for a TRIM–toluene mixture at a polymerization temperature of 80 °C. It can be seen that after a short induction period (about 1 min) the monomer consumption starts. The process proceeds slowly at first, and then after about 5 min, the rate increases rapidly. This behavior was also seen in the DSC measurements.[5]

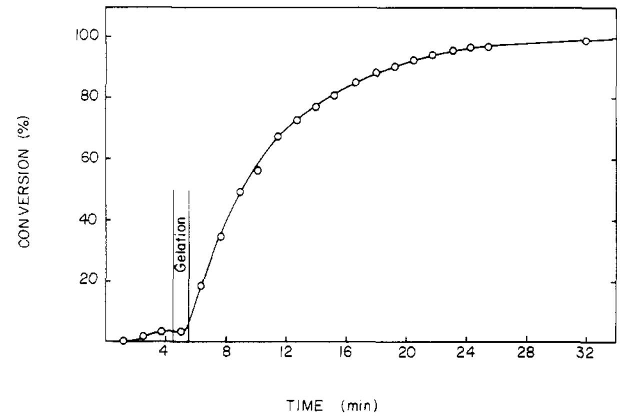

Figure 2. Influence of the polymerization time on the conversion of TRIM (temperature = 80 °C; monomer:solvent = 30:70; solvent = toluene). The interval where the gelation of the system occurs, according to visual observations, is marked by vertical bars.

Table I
Line Widths of the Methyl Group Belonging to Toluene Measured from ^1H NMR Spectra Collected during a TRIM Homopolymerization in the Presence of Toluene[a]

polym time, min	line width, Hz	polym time, min	line width, Hz
4.7	8.1	15.7	22.5
7.8	41.0	18.8	12.2
11.0	30.0	21.9	8.1

[a] Polymerization temperature = 80 °C.

Visual observation shows that the gelation of the system occurs after about 4.5–5.5 min of polymerization. The conversion was then unexpectedly low (about 3–4%). The gel formation in the system and the increase of the polymerization rate appear to coincide.

The drastic increase in the polymerization rate when the gel is formed is probably due to the gel effect (also known as the Norrish–Trommsdorf effect). The high conversion rate that occurs above this break point causes most of the polymerization to occur within the next 6–7 min (conversion = 70% after about 12 min).

When the conversion is greater than about 70%, the polymerization rate starts to decrease. After about 60–70 min of polymerization at 80 °C, no traces of monomer were detectable by NMR. The only peaks visible in the NMR spectra throughout the polymerization belong to the solvent. The area under the peaks was constant throughout the polymerization but their width varied with conversion.

The width of an NMR line depends upon the interaction of the studied group with neighboring groups.[6] In Table I the line widths belonging to the hydrogen of the methyl group in toluene are presented for different reaction times. It can be seen from the results that the line width increased abruptly after about 5 min of polymerization and reached a maximum (at about 5% conversion) and then decreased.

The maximum of the line width appears in the region where gelation occurs. As soon as a gel is formed the line width starts to decrease and at about 90% conversion it has the same value as originally. This could be explained by the occurrence of microsyneresis during the formation of large pores. The interaction between solvent and polymer in these pores would then be less pronounced. The measurements of line widths of a solvent present yet not taking part in the polymerization could therefore be used to predict the point of gelation.

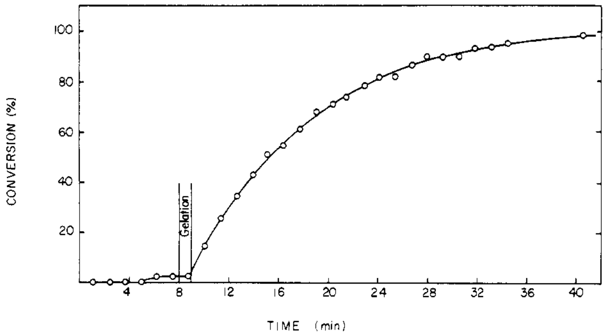

Figure 3. Influence of the polymerization time on the conversion of TRIM (temperature = 80 °C; monomer:solvent = 30:70; solvent = ethyl acetate). The interval where the gelation of the system occurs, according to visual observations, is marked by vertical bars.

The observed behavior of the line widths presented in Table I is also valid for the other peaks in the NMR spectra but because most of the peaks come from molecules that are taking part in the polymerization it is inconvenient to use these peaks for line-width measurements.

Changing the solvent from toluene, which has the same solubility parameter as poly(TRIM)[2] to ethyl acetate caused the rate of polymerization to decrease as shown in Figure 3. Traces of unreacted monomer (less than 1%) could be detected after about 70 min of polymerization at 80 °C. The induction period was longer but gelation occurred at about the same extent of reaction as in toluene. The gel formed was also more turbid than the gel formed in toluene.

Increasing the temperature affects the decomposition of the AIBN initiator and gives rise to a higher concentration of radicals in the system. The time for 90% conversion in experiments made at 80 °C was about 18 min. Increasing the temperature to 85 °C resulted in a decrease of the corresponding time to about 14 min. At lower temperatures (down to 70 °C) the rate decreased but the general shape of the conversion curve was the same.

Calculations of the kinetic order of reaction have also been made according to eq 8 in ref 5 for both homopolymerization systems studied. Similar results were obtained in both cases. Calculations for low degrees of conversions resulted in a kinetic order of reaction of about 1.4. For higher degrees of conversion the kinetic order of reaction decreased to about 1.0, which is similar to values obtained by DSC measurements.[5]

Kinetics of Copolymerization. In order to follow the conversion of MMA and TRIM during a copolymerization in a solvent (toluene or ethyl acetate), ^{1}H NMR experiments were performed in situ at 80 °C. The ^{1}H NMR spectrum for the TRIM–MMA–toluene mixture (Figure 4) also makes it possible to separately determine the concentration of the TRIM and the MMA molecules in the solution.

In Figure 5 the conversion of the two monomers [monomer/solvent = 30/70, solvent = toluene, the monomer composition is 20% MMA (v/v) and 80% TRIM (v/v)] is plotted against the polymerization time. In Figure 6 the same monomers were used but ethyl acetate was the solvent.

From Figures 5 and 6 it is evident that the rates of disappearance of TRIM and MMA are relatively similar. However, in ethyl acetate both monomers disappear at somewhat lower rate than in toluene.

Copolymerization was slightly faster than homopolymerization in both solvents. However, the difference in toluene was comparatively small while in ethyl acetate a considerable increase was observed. A reasonable ex-

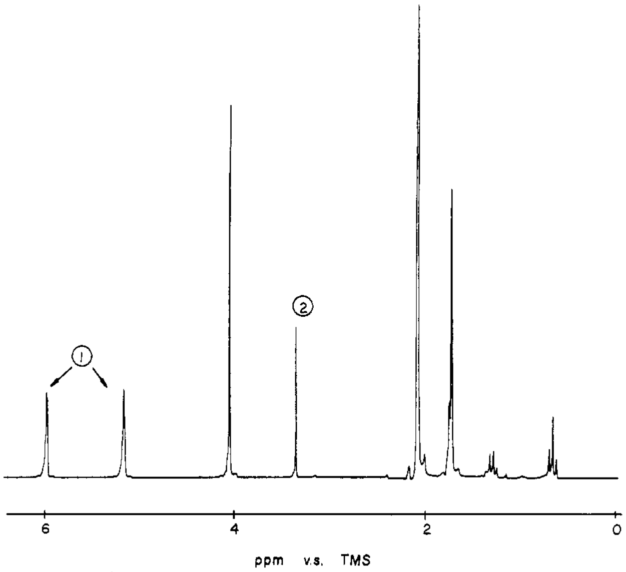

Figure 4. ^{1}H NMR spectrum from the TRIM–MMA–toluene system. The peaks marked with 1 represent the $=CH_2$ group in methacrylate and the peak marked with 2 represents the CH_3 group attached to the oxygen in the MMA molecule. These peaks have been used for the conversion measurements.

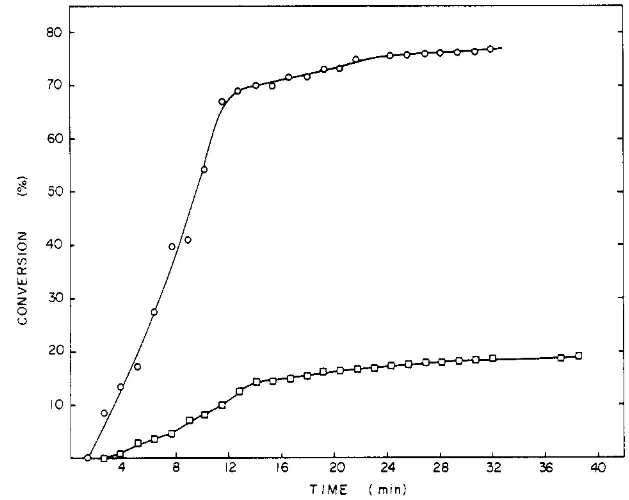

Figure 5. Influence of the polymerization time on the conversion of TRIM and MMA (temperature = 80 °C; monomer:solvent = 30:70; the monomer mixture consists of 80% TRIM and 20% MMA; solvent = toluene).

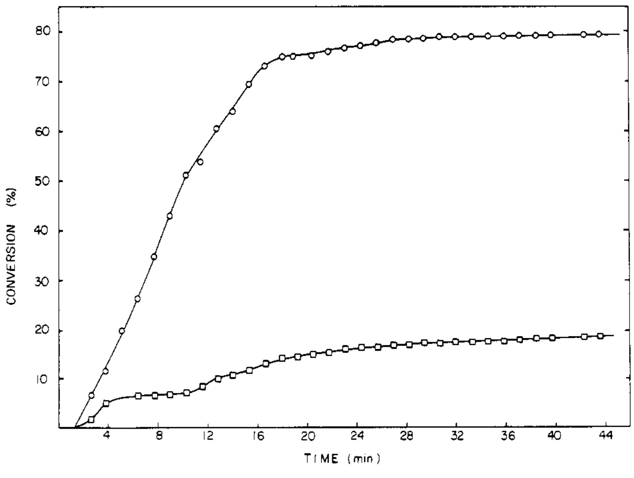

Figure 6. Influence of the polymerization time on the conversion of TRIM and MMA (temperature = 80 °C; monomer:solvent = 30:70; the monomer mixture consists of 80% TRIM and 20% MMA; solvent = ethyl acetate).

Table II
Amount of Unreacted Carbon–Carbon Double Bonds Present in Some Polymers Made at Different Temperatures Measured with Solid-State ^{13}C NMR Spectroscopy[a]

polym temp, °C	unreacted C=C, %	polym temp, °C	unreacted C=C, %
50	22.7	70	12.5
60	18.4	80	11.8

[a] Polymerization time = 4 h.

Table III
Amount of Unreacted Carbon–Carbon Double Bonds Present in Some Polymers Made with Varying Polymerization Times[a]

polym time, h	unreacted C=C, %	polym time, h	unreacted C=C, %
2	16.5	6	11.8
4	12.5	8	8.5

[a] The carbon–carbon double bonds were measured by solid-state ^{13}C FT-NMR spectroscopy (polymerization temperature = 70 °C).

planation is that copolymerization leads to a "looser" structure and hence better accessibility for the monomer. From Figure 5 it is also possible to conclude that the rate of addition of the two monomers is nearly the same. The reactivity ratios should then be about the same for both monomers.

Disappearance of Double Bonds. In order to investigate the influence of the polymerization time and temperature on the residual amount of unreacted carbon–carbon double bonds, TRIM was polymerized for 4 h at different temperatures and at 70 °C for different times. The results are presented in Tables II and III.

As can be seen from the results in Table II, an increase in the polymerization temperature decreased the amount of unreacted carbon–carbon double bonds in the resulting polymer.

When TRIM was polymerized in toluene it was not possible to detect any monomer molecules in the polymerization mixture after 120 min at 70 °C. From the results shown in table III, it is, however, possible to see that the amount of double bonds decreased when the polymerization time was increased from 2 to 8 h.

The observed behavior can be explained by the assumption that the pendant polymer double bonds participate in a polymerization reaction. This reaction is not rapid enough to produce heat that is detectable with DSC.[5] At higher temperatures the rate of radical formation and the rate of polymerization would be expected to increase as observed experimentally.

The reaction would then start with a radical attacking a pendant methacrylic group and react with it. The newly formed radical, which is bound to the polymer framework, would then attack a neighboring pendant methacrylic group and so on. This part of the reaction could be seen as the third step of the polymerization.

Conclusions

We have found that it is possible to follow the homopolymerization of TRIM as well as the copolymerization of TRIM–MMA in toluene or ethyl acetate through in situ measurements with ^1H NMR at elevated temperatures. We have also found that the gelation point of the TRIM–toluene system occurs near the break point in the conversion curve at low extents of reaction. We have also observed that it is possible to estimate the gel point by NMR line-width measurements of an inert component in the system.

An investigation of the influence of the polymerization time and temperature on the amount of unreacted carbon–carbon double bonds has also been performed. The number of double bonds were found to decrease with increasing polymerization time and temperature even after 100% monomer conversion.

The polymerization of TRIM could be divided into three discernible steps. The first step would then represent solution polymerization before the point of gelation. The second step represents the polymerization that occur between the point of gelation and 100% conversion of TRIM monomer, and the third step is the consumption of unreacted methacrylate groups on the solid poly(TRIM) network.

A kinetic order of reaction was calculated from conversion curves of the homopolymerization in toluene and ethyl acetate. The values calculated were the same for both solvents used. For low degrees of conversion, after the gel point, the kinetic order of reaction was found to be about 1.4 and for high degrees of conversion about 1.0.

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Registry No. TRIM, 3290-92-4; MMA, 80-62-6.

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