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^{13}C CP-MAS NMR Study on Content and Mobility of Double Bonds in Poly(trimethylolpropane trimethacrylate)

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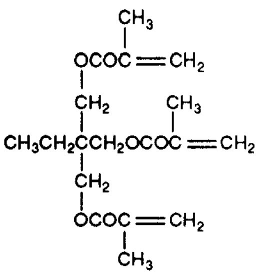
ABSTRACT: The content and mobility of unreacted methacrylic units in the polymer obtained from trimethylolpropane trimethacrylate, polyTRIM, has been investigated using solid-state NMR techniques. Porous particles of polyTRIM were prepared by suspension polymerization with toluene and isooctane as porogenic agents. The content of remaining double bonds was determined by cross-polarization magic angle spinning (CP-MAS) ^{13}C NMR. In unreacted units, the carbonyl resonance is shifted ca. 10 ppm upfield compared to the reacted units, due to conjugation with the carbon–carbon double bond. A detailed analysis of the cross-polarization behavior showed that quantitative results can be obtained. The amount of unreacted units, typically 0–15%, was found to depend on the polymerization parameters. Conditions favoring mobility, i.e., higher temperatures or increased solvent quality, resulted in lower content of residual double bonds. Bromine addition can also be used to determine the unreacted units, although the obtained values are somewhat higher than the NMR data. The reactivity toward bromine further indicates that the mobility is reasonably high. This has also been confirmed by measurements of the rotating-frame relaxation time constant, $T_{1\rho}(^{13}C)$. Most likely, $T_{1\rho}$ is dominated by spin–lattice processes; i.e., it can be interpreted in terms of molecular dynamics. The values obtained for C=O and $>C^*=CH_2$ in unreacted units are about twice that of C=O in reacted units, indicating increased mobility. The reactivity of the remaining double bonds in a radical polymerization with a chiral monomer was also demonstrated.

Introduction

Suspension polymerization is a common technique in commercial large-scale production of several polymers. It can also be used for the preparation of spherical particles for a broad range of applications where the spherical shape is an important prerequisite. One example is reactive macroporous particles, e.g., copolymers from glycidyl methacrylate (GMA) and ethylene dimethacrylate (EDMA)[1] or from styrene and divinylbenzene.[2] The polymer particles may be used for chromatography (GC, SEC, HPLC), in biological applications, and as catalyst carriers. In most applications it is desirable that the properties of the macroporous particles can be controlled within a narrow range during polymerization.

The purpose of this work has been to establish the conditions of preparation of reactive macroporous particles from trimethylolpropane trimethacrylate (TRIM). The structure of TRIM with three double bonds



will ensure that the cross-linking density of polyTRIM is very high. Suspension polymerization of TRIM can be used to obtain macroporous particles, and due to the cross-linked network these particles will contain unreacted double bonds as reactive groups. Besides particle size and porosity, amount and availability of the double bonds are some of the most important parameters of these particles.

There are a number of methods for the detection of carbon–carbon double bonds: IR,[2–5] Raman spectroscopy,[6] and chromatography together with the formation of Pt(II) complexes[5] and addition of bromine.[7,8] The high cross-linking density of polyTRIM and its rich IR spectrum make these analyses quite difficult. With the advent of high-resolution solid-state NMR (CP-MAS NMR), a powerful technique to analyze insoluble polymers has, however, become available. In an unreacted acrylate group the carbonyl bond is conjugated with a double bond, which should shift the ^{13}C carbonyl resonance about 10 ppm upfield compared to the reacted units. This has indeed also been used to determine the amount of unreacted units in several different polymers obtained from multifunctional acrylates and methacrylates[9–11] including TRIM.[12]

We have investigated the polymerization conditions, e.g., temperature, type of porogenic agent, and degree of conversion, with respect to their influence on the amount of unreacted double bonds. To determine the double bonds, we have used ^{13}C CP-MAS NMR. The results obtained using this method are also compared with results obtained with the standard bromine addition method. The possibility of utilizing different relaxation parameters obtained in the NMR measurements to study the mobility of the unreacted units is discussed as well.

Experimental Section

Materials. Technical-grade quality of TRIM, obtained from Degussa containing 90% pure TRIM and 10% mono- and disubstituted TRIM, was used as monomer. Toluene (pro analysis, BDH) and isooctane (puriss, Merck) were used as poro-

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genic agents. Bromine (pro analysis, Merck) and carbon tetrachloride (pro analysis, Rathburn) were used to prepare the bromine solution. All other chemicals were of analytical grade and used without further purification.

Polymerization. The polymerization experiments, which will be described in detail in a forthcoming paper,[13] were performed in a 200-mL reactor vessel, consisting of a glass mantle with a steel top and bottom, sustaining pressures up to 2 MPa. The reactor is similar to the setup previously described by Nilsson et al.[14] The reactor was equipped with a thermistor for calorimetric measurements, a heating element used for calibration purposes, and a four-bladed propeller with a diameter of 35 mm. The preparation of the porous particles was carried out by suspension polymerization at 60, 70, and 90 °C.

At 100% conversion, as judged from the calorimetric measurements, the polymerization product was obtained in the form of spherical particles with particle sizes of 20–150 μm. The polyTRIM particles were swollen in toluene and washed successively with toluene, ethanol, and water, followed by drying at 60 °C in vacuo. The product from polymerizations with lower conversion, 50–80%, consisted of porous, spherical 20–150-μm particles, as well as grains with sizes on the order of 130 nm. In order to isolate the particles, a glass filter with pore size of 41–100 μm was used. The product was washed successively as described above.

Determination of Double Bonds. Single-contact ^{13}C CP-MAS NMR spectra[15-17] were obtained at 50.3 MHz using a Varian XL200 spectrometer equipped with an auxiliary high-power amplifer and a solid-state probe with magic angle spinning capability. This spectrometer employs a two-level decoupling scheme with a proton B field of ca. 5.8 and 12 G during cross polarization and acquisition, respectively. The Hartmann–Hahn condition[18] and the magic angle were adjusted by using the aromatic signal of hexamethylbenzene.

The samples were packed in a Kel F rotor, which was spun at ca. 3 kHz. The spectra were obtained in a 16-kHz window using 4K time-domain data points. Before transformation the free induction decays were zero filled. Chemical shifts were calibrated via external reference to the aromatic carbon of hexamethylbenzene (132.1 ppm relative to TMS). Typically 5–6000 scans were accumulated to obtain each spectrum. Variable contact time as well as interrupted decoupling ($T_{1\rho}$(^{13}C) measurements) experiments were also performed. For each spectrum 1000 scans were accumulated repeatedly cycling through the different time values, adding 100 free induction decays each time. By this interleaving procedure possible errors from long-term changes in spinner speed, amplifier power, and magic angle setting are minimized.

The addition of bromine to carbon–carbon double bonds was used as a simple reference method to the ^{13}C CP-MAS NMR method. A solution of 10 mL (0.13 mol/L) of bromine in CCl_4 was added to 0.5 g of polyTRIM particles in a test tube. The added solution contained about a 3-fold molar excess of bromine calculated on the assumption that about 10 mol % of unreacted methacrylic units were left after the polymerization. The test tube was shaken vigorously for a few minutes and allowed to react for at least 24 h at room temperature. After completed reaction time, the sample was placed on a glass filter and washed with approximately 500 mL of CCl_4, 300 mL of toluene, 200 mL of acetone, and 50 mL of diethyl ether. The sample was finally dried overnight at 60 °C. The weight percent of reacted bromine was determined by elemental analysis. Assuming that two bromine atoms are added to one carbon–carbon double bond, the mole percent of unreacted methacrylic groups was calculated.

Results and Discussion

The polymerization rate of TRIM was followed by the calorimetric reactor. Figure 1 shows the polymerization rate of TRIM in toluene at 60 °C. According to the calorimetric measurements, 100% conversion was reached after 100 min.[13] The heat of polymerization, ΔH, was calculated to 105 kJ/mol. When this value of ΔH is used, it was possible to calculate the degree of conversion at different reaction times. The polymerization reaction could be stopped at required conversions by cooling and adding inhibitor.

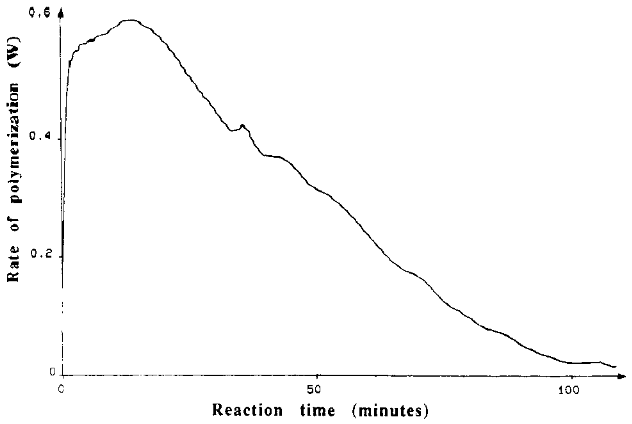

Figure 1. Example on recording from the calorimetric reactor: polymerization temperature, 60 °C; toluene as porogenic medium.

The morphology of the product was studied by scanning electron microscopy, SEM. At low conversion, we noticed a high content of grains (particles less than 1 μm in diameter). At 50% heat conversion the polymer product consisted of 56 wt % particles and 44 wt % grains. The content of grains was reduced to 25 wt % at 80% heat conversion. It seems that the grains consume double bonds in building up the particles. The content of unreacted double bonds in the particles at different conversions, see below, indicates that the content of double bonds is larger in the grains.

The ^{13}C CP-MAS NMR spectrum of a sample of polyTRIM is given in Figure 2. For comparison the spectrum of solid PMMA and the solution spectrum of TRIM are included as well. The assignments of PMMA are those given in the literature.[19] For the monomer the assignments were obtained by the combination of simple additive effects on chemical shifts and the coupled spectrum. In most cases the assignments of polyTRIM can then be obtained by a simple comparison; see Figure 2. These assignments are in accordance to earlier published ones for polyTRIM and similar systems.[9-12]

Some of the peaks are substantially broader than the majority. For methacrylates in solution stereochemical configurations are manifested most clearly by splitting of the $-CH_3$ and $-CH_2-$ resonances, which are seen as broader peaks in the spectrum of polyTRIM (peaks 12 and 6, respectively). Resonance 5 is also substantially broadened, but this is an effect of reduced mobility rather than different stereostructures. This carbon, $-CH_2O-$, is part of the cross-linking points, and it is also protonated. If the frequency of its motion and that of the decoupling field (ca. 40 kHz) are comparable, the suppression of the dipolar decoupling becomes inefficient, leading to broadening.[20,21]

It is of course of special interest to note the changes caused by reaction of the double bonds. Signals 2–4 and 11 are those that are most influenced, i.e., the olefinic carbons, the carbonyl, and the α-CH_3 group. Instead some new signals will appear, nonconjugated C=O (178 ppm compared to 168 ppm) and $-CH_2-$ in the main chain at ca. 55 ppm, and finally α-CH_3 is moved to ca. 20 ppm. With regard to the determination of residual unsaturation, resonances 11, 8, and 6 could in principle be used, but this is prevented by severe overlap. Both the olefinic carbons and the carbonyl in methacrylate units are, however, well separated from other resonances and should be possible to use. Due to similarity in structure, as well

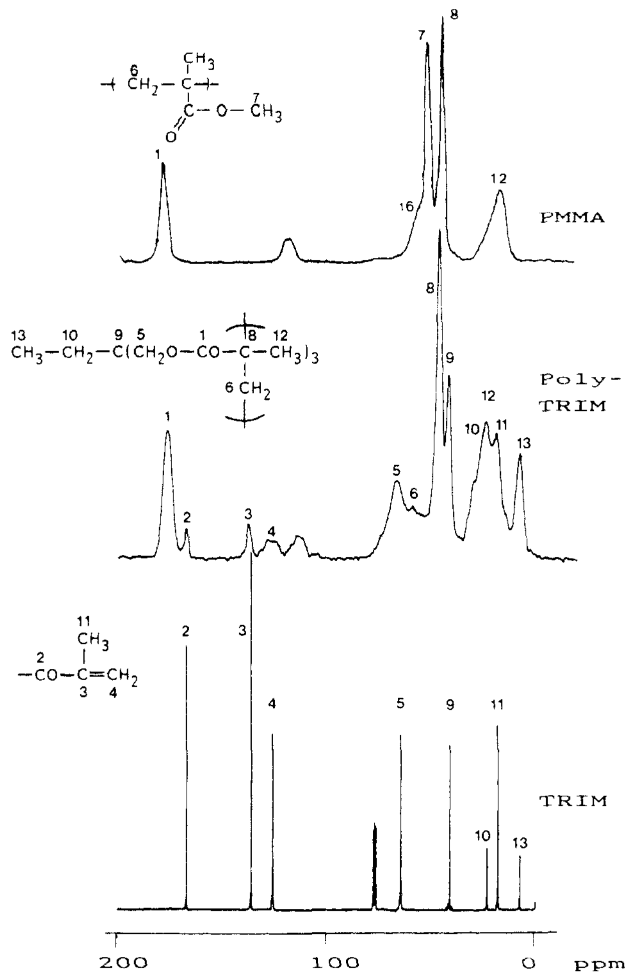

Figure 2. ^{13}C CP-MAS NMR spectra of polyTRIM and PMMA and solution ^{13}C NMR spectrum of TRIM.

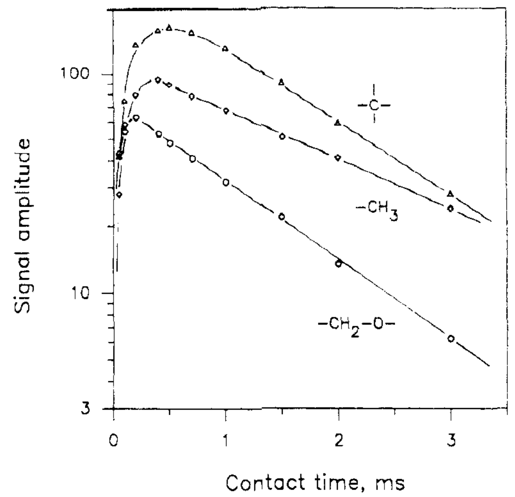

Figure 3. Variation of the ^{13}C NMR signal during cross polarization; peaks 5, 8, and 12 in Figure 2.

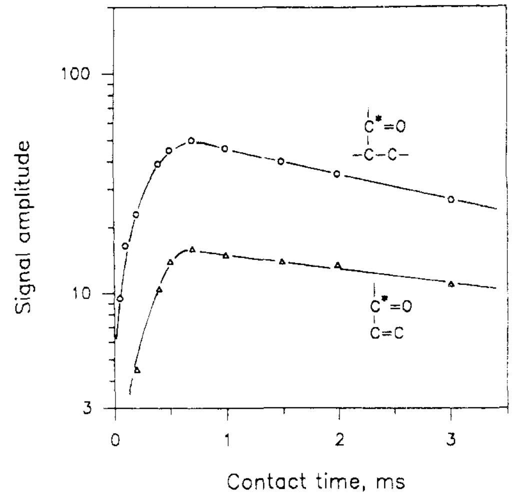

Figure 4. Variation of the ^{13}C NMR signal during cross polarization; peaks 1 and 2 in Figure 2.

as the potential risk for overlap with spinning sidebands in the case of the olefinic carbons, we have concentrated our work on the carbonyl resonances.

Quantification in CP-MAS NMR spectra, however, is not straightforward. The ^{13}C NMR signal in solid-state NMR is enhanced by cross polarization,[15,18] in which magnetization is transferred from ^1H to ^{13}C spectra normally by a Hartmann–Hahn contact. The possibility of quantifying the results will therefore depend on the kinetics of the transfer of magnetization. The coupling between ^{13}C and ^1H spectra occurs via dipole–dipole interactions. As the latter has a $1/r^6$ dependence upon the distance r between ^{13}C and ^1H spectra, the intensity of different lines will rise with different speeds: carbons without directly bonded hydrogen cross polarize much more slowly than H-substituted carbons. The higher mobility of methyl groups (free rotation around the ternary axis) reduces the dipolar interaction so that methyls behave similarly to CH groups. As the cross polarization depends on static interactions,[20] the signal buildup will generally be faster if the rigidity is increased.

The rise in ^{13}C magnetization is counteracted by another process: reduction of the proton magnetization due to relaxation of the protons in the rotating coordinate system with the time constant $T_{1\rho}(^1H)$. The signal intensity will therefore pass through a maximum. The contact time to obtain the maximum is most often different for different carbons in the same molecule. To be able to obtain quantitative data, the cross-polarization behavior must be determined and, if necessary, corrected for.

Some examples of the cross-polarization behavior are shown in Figure 3. As expected the signal buildup for the quaternary carbon (47 ppm) is relatively slow due to the weak carbon–proton dipolar interaction for non-proton-bonded carbons. In the case of the $-CH_2O-$ carbons at 66 ppm the rise of the magnetization is much faster. The rise time to half of the total population, $t_{1/2}$, is in fact only 18 μs, which is indicative of rigid-lattice behavior.[20] In contrast, the intensity of the signal of the methyl group at 19 ppm increases somewhat slower. Although the three protons should contribute to an efficient cross polarization, the process becomes slower due to partial motional averaging of the dipolar interaction between the carbon and its bonded hydrogens. Most signals, except that of the methyl groups, show a parallel decay representing a proton rotating-frame relaxation time constant $T_{1\rho}(^1H) = 1.3 \pm 0.1$ ms. This is consistent with rapid rotating-frame proton spin diffusion between sites with different mobility.

The behavior of the carbonyl resonances is of special interest. The signal buildup of these resonances is again slower, see Figure 4, as these carbons are nonprotonated. Both resonances reach maximum intensity at the same contact time, 700 μs. The decay is even slower than those for the methyl groups; $T_{1\rho}(^1H) = 8.5$ and 3.7 ms for the resonances at 168 and 178 ppm, respectively. This indicates that the carbonyl carbons are not influenced by the rapid rotating-frame proton spin diffusion in contrast to the neighboring quaternary carbon. Most important is that the decay is similar for both resonances. To obtain maximum signal intensity, 700 μs was used for the quantitative measurements. The similar cross-polarization behavior indicates that the integrated areas of the two carbonyl resonances might be used directly for the quantitative evaluation, at least as a first approximation. To obtain a more correct count of the spins, these values should, however, be multiplied with a scaling factor $\lambda/f(t)$, eqs 1 and 2, which takes T_{CH} (time constant for polarization of carbons), $T_{1\rho}(^1\mathrm{H})$, and $T_{1\rho}(^{13}\mathrm{C})$ (time constant for carbon relaxation in the rotating frame) into account.[22]

$$\lambda = 1 + \frac{T_{\mathrm{CH}}}{T_{1\rho}(^{13}\mathrm{C})} - \frac{T_{\mathrm{CH}}}{T_{1\rho}(^{1}\mathrm{H})} \tag{1}$$

$$f(t) = \exp\left(-\frac{t}{T_{1\rho}(^{1}\mathrm{H})}\right) - \exp\left[-t\left(\frac{1}{T_{\mathrm{CH}}} + \frac{1}{T_{1\rho}(^{13}\mathrm{C})}\right)\right] \tag{2}$$

The carbon relaxation time constant in the rotating coordinate system, $T_{1\rho}(^{13}\mathrm{C})$, can be determined in interrupted decoupling experiments, see below. The variable contact time experiments can then be used to obtain T_{CH} as well as $T_{1\rho}(^1\mathrm{H})$.[22] The scaling factor, $\lambda/f(t)$, for a contact time t = 700 μs could be calculated to 1.15 and 1.25 for the carbonyl carbon in unreacted and reacted units, respectively. If the values obtained by integration of the two signals are used without any correction, the calculated amount of unreacted units will thus be ca. 10% too high.

Figure 5 shows some examples of CP-MAS NMR spectra of polyTRIM. It is obvious that the amount of unreacted double bonds decreases from the top to the bottom spectrum; the relative intensity of the carbonyl peak due to the unreacted units (168 ppm) decreases. Although other changes can be observed, none of these would allow more than a qualitative statement about the degree of conversion; see, e.g., the resonance at 11 ppm due to α-$\mathrm{CH_3}$ in unreacted units. The magnification demonstrates the good resolution between the two carbonyl resonances, which allows a simple quantitative evaluation by integration. Note that the intensities cannot be used due to the large differences in line widths; $\Delta\nu_{1/2}$ is ca. 280 Hz for the carbonyl in reacted units but only ca. 100 Hz for the unreacted ones. The increased broadness is a result of the restricted mobility imposed by the cross-linking process. Besides the increased possibility for this carbon to experience different environments, decreased efficiency of the dipolar decoupling (see above) might be an important reason.

Table I presents data on polyTRIM prepared in the interval 60–90 °C using toluene or toluene with 20% isooctane as reaction media. In all cases the conversion was 100% according to the measurements of heat of reaction. It is, however, obvious that the polymers still contain a substantial amount of unreacted methacrylate groups. It must be remembered that 100% cure in measurements based on the heat of reaction is assumed when no further exothermic reaction can be detected. Similar results have been reported for different diacrylates[10] as well as TRIM.[12]

In their work Allen et al.[10] also argued that polydiacrylates contain free unreacted *monomer*, which, in contrast to unreacted double bonds in monomeric units already linked to the network, does not contribute to the CP-MAS NMR spectrum. The reason for this should be that fast isotropic molecular tumbling precludes cross polarization in the case of free monomer. If this should be applicable for polyTRIM as well, the total amount of unsaturation would be higher than the values in Table I. In a recent work[23] it has, however, been stated that free monomer cannot be detected after about 75% conversion in polymerization of TRIM. In the latter case ^{1}H NMR in situ measurements were used to detect the amount of remaining monomer, thus utilizing the higher mobility of free monomer. Nor did preliminary experiments in our laboratory using a ^{13}C $\pi/2$ pulse and MAS but no CP give any evidence of free monomer for a sample with 8% unreacted methacrylic units (CP-MAS).

The phenomena of entrapment of unreacted double bonds in cross-linked polymers has been reported for other polymers as well, e.g., styrene–divinylbenzene copolymers.[24] It is, however, obvious that the ultimate cure depends on the reaction conditions; see Figure 6. With increasing temperature the amount of unreacted methacrylic groups in the TRIM particles decreases. This is probably due to increased diffusion rate of the monomer mol-

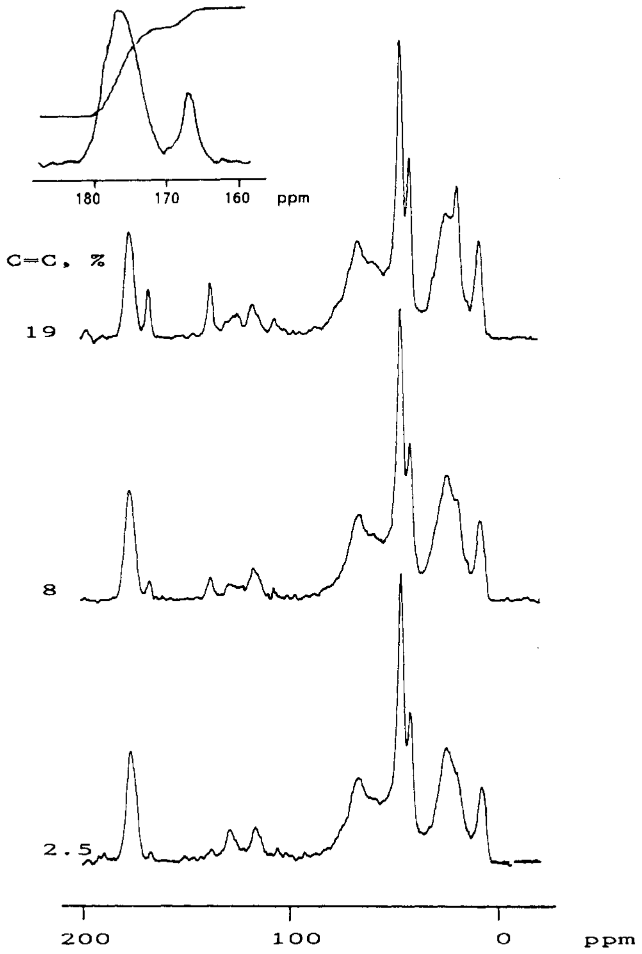

Figure 5. ^{13}C CP-MAS NMR spectra of polyTRIM obtained under different conditions resulting in different amounts of unreacted methacrylic units.

Table I
Effect of Polymerization Conditions on the Amount of Unreacted Methacrylic Groups after Polymerization to 100% Conversion[a]

polymerizn temp, °C	reaction medium		fraction of unreacted units,[b] mol %
	toluene	isooctane	
60	1		8.4
60	0.8	0.2	9.3
70	1		6.0
70	0.8	0.2	7.1
90	1		2.7
90	0.8	0.2	3.2

[a] Calorimetric measurements. [b] CP-MAS NMR.

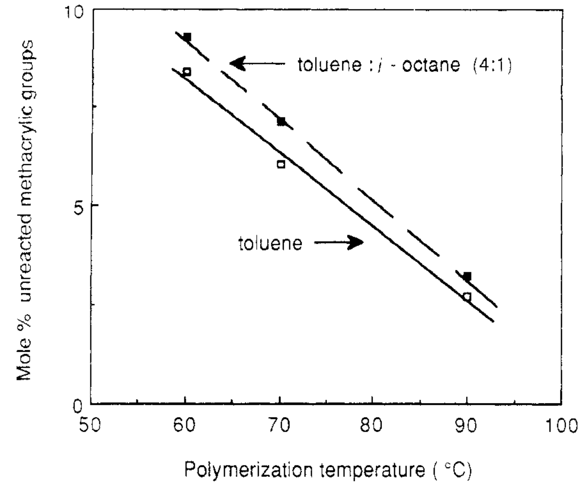

Figure 6. Amount of unreacted methacrylic groups (^{13}C CP-MAS NMR) in polyTRIM particles, as a function of polymerization temperature and solvent system.

Table II
Effect of Postpolymerization of Low Conversion Products[a] after Removal of Grains and Free Monomer

sample	fraction of unreacted units,[b] mol%
50% convn[c]	16.7
after postpolymerizn	13.0
70% convn[c]	14.0
after postpolymerizn	7.4

[a] 60 °C, toluene. [b] CP-MAS NMR. [c] Calorimetric measurements.

ecules and to an increased mobility for the polymer segments in the particles. Changing the solvent in the polymerization from toluene to toluene with 20% isooctane leads to an increase in the content of unreacted groups, Figure 6. The solvent power of isooctane is lower than that of toluene, which means that the TRIM particles will be less swollen in the mixed solvent. The mobility of the segments will thus be lower; i.e., decreased solvent power would effect ultimate cure in the same way as decreased temperature in accordance with the observations.

An extrapolation of the curve obtained with toluene as the reaction medium indicates that complete reaction of all double bonds would be achieved at ca. 110 °C. The mobilities of the unreacted groups are thus relatively high, although they are connected to a very densely crosslinked structure. It is, however, not possible to completely ignore the presence of free monomer. In order to check the reactivity of unreacted groups, two runs were stopped at 50 and 70% conversion, respectively, according to the calorimetric measurements. The product obtained from the reactor was worked up according to the procedure outlined in the Experimental Section, i.e., separation of grains and careful washing with different solvents in order to remove free monomer. The amount of unreacted methacrylate groups was determined by CP-MAS NMR; see Table II. The values indicate a much higher degree of conversion than that given by the calorimetric data. It must be remembered, however, that eventual free monomer has been removed from the particles. It is, furthermore, possible that the content of unreacted groups in the grains can be considerably higher than that in the particles. The isolated particles were then subjected to a "postpolymerization" involving swelling with solvent, heating to 60 °C, and the presence of a radical initiator. This treatment led to a continued polymerization between the pendent methacrylic groups as evidenced by the decreased amount of double bonds, Table II.

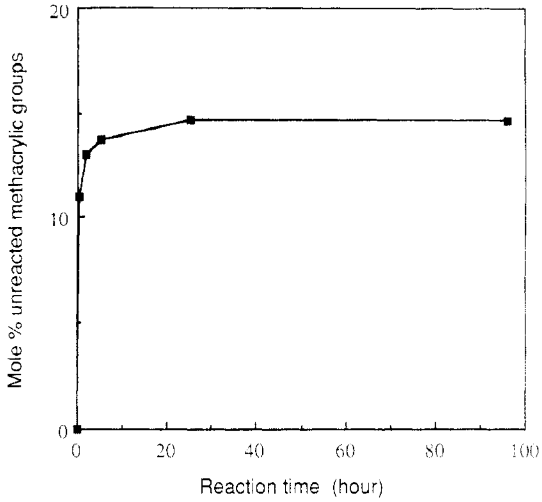

Figure 7. Degree of bromine addition to polyTRIM given as the content of unreacted methacrylic groups, as a function of the reaction time with bromine; polymerization temperature, 60 °C; toluene as solvent.

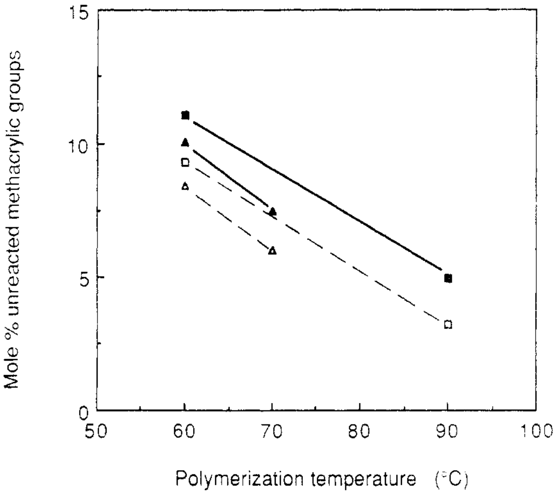

Figure 8. Amount of unreacted methacrylic groups, analyzed by both ^{13}C CP-MAS NMR and bromine addition, as a function of polymerization temperature and solvent system: closed symbols, bromine addition; open symbols, NMR; ▲, △, toluene; ■, □, toluene–isooctane (4:1).

The mobility of the pendent methacrylic groups is thus high enough to allow an internal reaction. The possibility for these double bonds to react should be even higher if a low molecular reactant was introduced. One example is addition of bromine, which we have tested as a possibility to determine the amount of unreacted groups. Although bromine is quite large, the reaction was reasonably fast even at room temperature; see Figure 7. A comparison of the results obtained with bromine addition and CP-MAS NMR shows that the former always gave 2–3 mol % higher values; see Figure 8. One possibility could be that the TRIM particles contain free monomer, which would be detected by bromination but not in the NMR measurements. According to the discussion above, it is, however, less likely that free monomer is present at the high levels of conversion in question. The constant difference between the two methods is another argument; with an increasing degree of conversion, the difference should decrease.

Another possibility is that the bromination values are too high due to unspecific surface absorption. The results

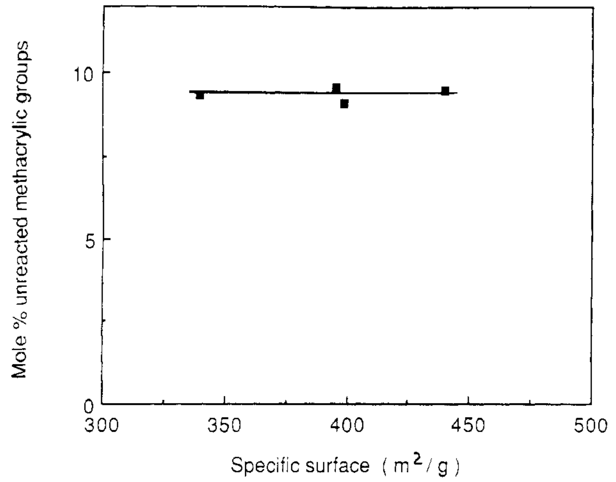

Figure 9. Degree of bromine addition to polyTRIM particles, given as content of unreacted methacrylic groups, as a function of the specific surface area of the polyTRIM particles.

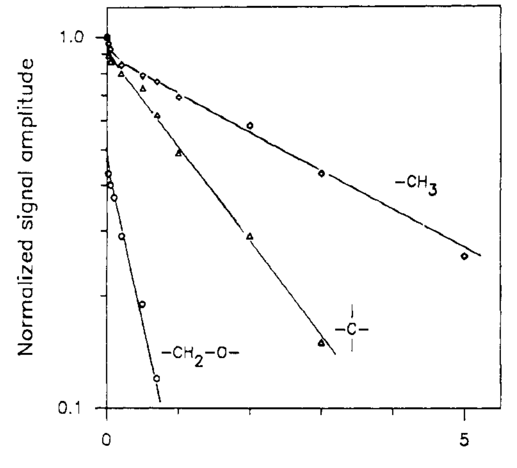

Figure 10. $T^*_{1\rho}(^{13}C)$ measurement of polyTRIM: content of unreacted units, 9.3%; peaks 5, 8, and 12 in Figure 2.

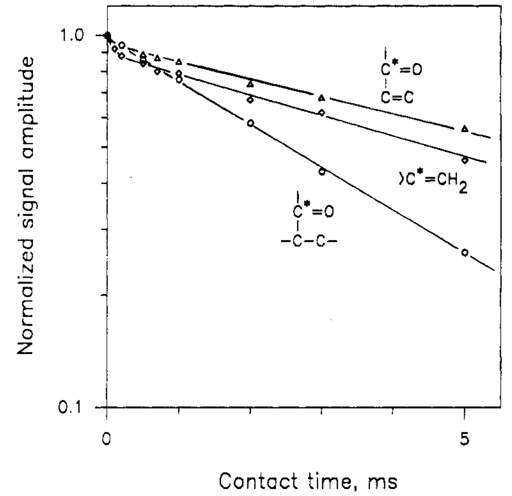

Figure 11. $T^*_{1\rho}(^{13}C)$ measurement of polyTRIM: content of unreacted units, 9.3%; peaks 1–3 in Figure 2.

from bromine addition on a series of TRIM particles with different specific surface area, see Figure 9, do, however, not show any relationship between the amount of analyzed bromine and the surface area. The different TRIM particles used to obtain the results in Figure 9 were prepared under identical conditions apart from the ratio between toluene and isooctane, which influences the specific area of the particles. The amount of unreacted methacrylic groups will, however, be effected as well, see Figure 6, and in order to minimize this effect the particles were "postpolymerized" as described above.

The difference could more likely be explained by bulk absorption of bromine. The bromination is performed in a slurry with carbon tetrachloride as the medium. The TRIM particles are swollen, which, of course, increases the accessibility for bromine. After reaction the particles are filtered off and washed with different solvents in a series with decreasing swelling capacity. If unreacted bromine remains after washing with CCl_4 and toluene, the decreased swelling will decrease the diffusion rate of bromine and could ultimately lead to "permanent" inclusion of bromine in the dense network.

It is also possible to study the mobility of the different structures by several NMR relaxation time constants. Two of these, T_{CH} and $T_{1\rho}(^1H)$, have been discussed earlier. Another parameter that could be used is the time constant for carbon relaxation in the rotating frame, $T_{1\rho}(^{13}C)$, which can be determined by interrupted decoupling experiments. Molecular motions with a spectral component at the frequency determined by the cross-polarization radio-frequency field strength (in the mid-kilohertz region) are of crucial importance for this relaxation.[25]

The results of the interrupted decoupling experiments for some structures are presented in Figures 10 and 11. It is obvious that the measured $T_{1\rho}(^{13}C)$ values show a large differentiation. It is interesting to note that the value of carbonyl carbons in unreacted units is more than twice that of reacted ones and that $T_{1\rho}(^{13}C)$ of the nonprotonated olefinic carbons is very similar to that of the neighboring carbonyl carbon. The interpretation of $T_{1\rho}(^{13}C)$ data is, however, complicated as the relaxation in the rotating frame is caused by fluctuating dipole fields of protons. The fluctuation can be caused by reorientation of the C–H bond vector, i.e., due to rotational diffusion of the group in question. This is the so-called spin–lattice relaxation, which can be related to molecular dynamics. The measured $T^*_{1\rho}(^{13}C)$ consists, however, of two possible components, the spin–lattice relaxation and a possible spin–spin contribution T^D_{CH},[25,26] eq 3.

$$\frac{1}{T^*_{1\rho}(^{13}C)} = \frac{1}{T_{1\rho}(^{13}C)} + \frac{1}{T^D_{CH}} \qquad (3)$$

The spin–spin relaxation is caused by fluctuations in dipole fields generated by changes of the spin state of protons close to carbons; i.e., this process is not influenced by molecular dynamics. If the measured $T^*_{1\rho}(^{13}C)$ values should be interpreted in terms of molecular dynamics, it must be proven that $T^D_{CH} \gg T_{1\rho}(^{13}C)$. It is possible to determine T^D_{CH} separately,[26] but such measurements are lengthy and were not performed in this study.

It has been shown that rotating-frame relaxation in amorphous polymers, e.g., polystyrene, poly(methyl methacrylate), poly(phenylene oxide), poly(ethylene terephthalate) and polycarbonate, is dominated by spin–lattice processes and that, consequently, $T^*_{1\rho}(^{13}C)$ can be interpreted in terms of molecular dynamics.[27] Even for a cross-linked amorphous polymer such as cured epoxy, the relaxation has at least predominately been related to spin–lattice processes.[28] On the other hand, for rigid polymers with strongly coupled protons, in particular crystalline systems such as polyethylene[29] and polyoxymethylene,[30] spin–spin relaxation is more important.

It should therefore be possible to interpret the $T^*_{1\rho}(^{13}C)$ data of polyTRIM in terms of molecular mobility, at least as a first approximation. One clear example of the influence of molecular motions can be noticed in the case of the $-CH_2O-$ carbon. The low $T_{1\rho}(^{13}C)$ value (0.55 ms) is in agreement with the motional line broadening for these carbons discussed above. Similar behavior has been observed for the corresponding carbons in poly(butyl acrylate) at 283 K[21] and poly(cyclohexyl methacrylate).[20] In fact, $\Delta\nu_{1/2}$ can be estimated to ca. 500 Hz, which indicates the equality $T_{1\rho}(^{13}C) \approx T_2$. Therefore, the observations point out that the rate of molecular motions is equal to the carbon irradiation field strength in frequency units,[22,31,32] i.e., rather slow molecular motions. The somewhat longer value for the quaternary carbon at 47 ppm is expected as nonprotonated carbons are less strongly coupled to ^1H spectra. The rather long $T^*_{1\rho}(^{13}C)$ of CH_3 is due to rotation about the ternary axis and corresponds to the cross-polarization behavior of CH_3 groups.

The carbonyl carbons in the reacted units have about the same $T^*_{1\rho}(^{13}C)$ as the methyl groups, 3.7 and 4.1 ms, respectively. This equality together with a low value for $-CH_2O-$, as well as values very similar to those obtained in the present investigation, has been reported for poly(butyl acrylate) below the glass transition.[21] In that case it was shown that the rotating-frame relaxation could be related to molecular mobility. The similarity in overall structure and conditions, in our case, a polymethacrylate below T_G, further supports our assumption that the relaxation data of polyTRIM can be interpreted in terms of molecular mobility.

In many potential applications for polyTRIM particles it is of interest to use the unreacted methacrylate groups to graft an active component. The most important aspect of molecular mobility of this material is therefore the mobility, and thus the accessibility, of these groups. The fact that $T^*_{1\rho}(^{13}C)$ values of both C=O and $>C^*=CH_2$ in unreacted units (8.5 and 7.6 ms, respectively) are about twice that of C=O in reacted units (3.7 ms) indicates that the spin-lattice relaxation of the former is considerably slower; i.e., the spectral density in the midkilohertz region is much smaller. Most reasonably, this is due to increased mobility manifested by a higher frequency motion. It is, however, necessary to consider the possibility that the relaxation of these carbons is influenced by spin-spin processes to a higher degree than the other carbons. The cross-polarization behavior of these carbons was quite unusual as the value of $T_{1\rho}(^1H)$ for considerably longer than for the other carbons. Normally all carbons in a homogenous sample, including nonprotonated, have the same $T_{1\rho}(^1H)$ due to rapid spin-spin diffusion among the protons. The slower decay of the magnetization of the carbonyl carbons indicates that these in fact are less influenced by proton spin-spin processes. The carbon relaxation in the rotating frame should thus be equally well dominated by spin-lattice relaxation. The larger $T_{1\rho}(^{13}C)$ values of C=O in unreacted units, compared to that of reacted ones, can thus be explained by higher mobility of the former. A high degree of mobility is also in agreement with the reactivity of these groups, e.g., demonstrated by the bromination.

We have also tested the use of the double bonds to graft a chiral polymer onto polyTRIM. The monomer used was *N*-acroyl-(*S*)-phenylalanine ethyl ester, and the intention is to obtain a column material for enantiomeric separation. The chromatographic results will be described in another paper,[33] but the CP-MAS NMR spectrum will be discussed here.

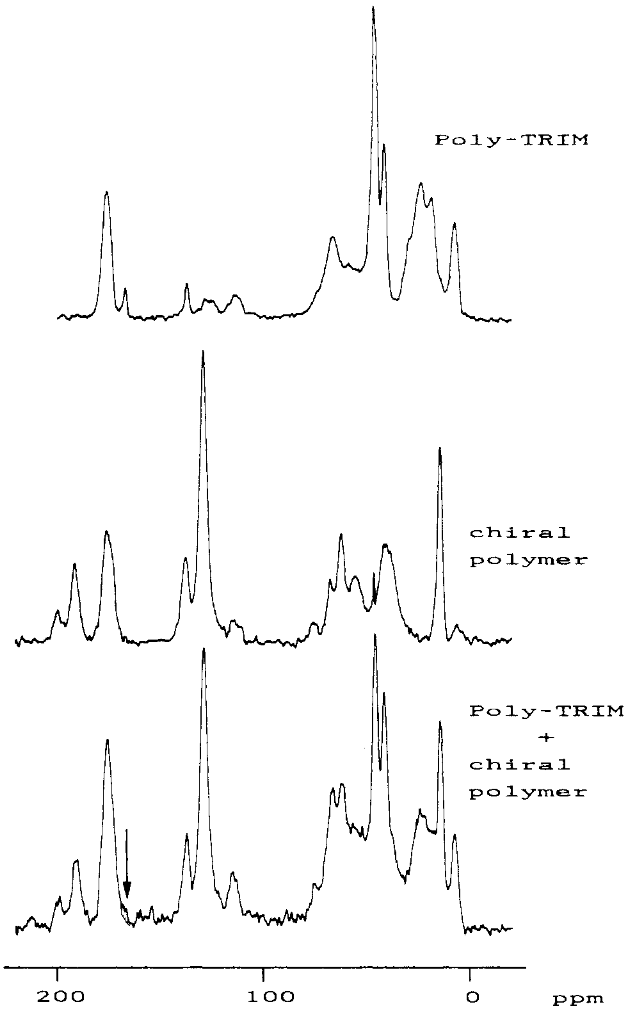

Figure 12. ^{13}C CP-MAS NMR spectra of polyTRIM, linear chiral polymer, and the product obtained by polymerization of the chiral monomer inside polyTRIM particles.

The two top spectra in Figure 12 represent a sample of polyTRIM, with 12% unreacted methacrylic groups, and the linear polymer obtained by polymerization of chiral monomer. Most of the assignments for the latter are quite obvious: 177 ppm, ester and amide C=O; 138 and 128 ppm, aromatic carbons; 64 ppm, $>CHNH-$; 58 ppm, $-CH_2O-$; 35–45 ppm, $PhCH_2-$, and main-chain $-CH_2CH-$; 14 ppm, $-CH_3$. It can be noted that the $-CH_2O-$ carbons show a much sharper signal in the chiral polymer than in polyTRIM. This is what could be expected as the mobility of the former should be higher: (1) it is a polyacrylate and not a polymethacrylate, and (2) it is not cross-linked.

The bottom spectrum represents the graft copolymer obtained by polymerizing the chiral monomer swelled into polyTRIM particles. After the reaction the particles were washed thoroughly in order to remove unreacted chiral monomer and linear chiral polymer. Except for some of the broader peaks, most peaks from polyTRIM and the linear chiral polymer can still be seen. In comparison to polyTRIM, the C=O peaks in the chiral polymer are shifted somewhat upfield, in particular, the amide carbonyl (ca. 174 ppm). The separation between the major C=O peak and that due to C=O in unreacted methacrylic groups is therefore less good than that in polyTRIM. However, a small shoulder (shadowed in the figure) can be seen at the expected shift, 168 ppm, and we consider this to represent remaining double bonds in polyTRIM. A quantification is of course difficult, but we estimate the shadowed area to represent 2–5% of the carbonyls in polyTRIM.

The spectrum of the graft product does not show any peaks from the graft points. It could, therefore, equally well be a mixture of polyTRIM and the chiral polymer. The graft polymerization was, however, performed at the same temperature as that used to prepare the polyTRIM. The remaining double bonds, see top spectrum in Figure 12, thus represent the ultimate conversion at the temperature in question.

Obviously, the presence of the chiral monomer has facilitated further reaction of the double bonds, most likely in a grafting process. A preliminary $T_{1\rho}(^{13}C)$ investigation has also shown that some of the relaxation time constants of the chiral polymer resonances are different for the linear polymer compared to the corresponding ones of the graft product. Although a more detailed study is called for, this is a further indication that grafting indeed has occurred.

Conclusions

The polymerization of TRIM leads to a densely crosslinked network. Although calorimetric measurements show that ultimate conversion has been reached, ^{13}C CP-MAS has shown that there still are unreacted methacrylic units present. The best resolution was obtained for the carbonyl resonance, which is shifted ca. 10 ppm upfield due to conjugation with the carbon–carbon double bond. Variable contact time experiments showed that the cross-polarization behavior of the two kinds of carbonyls are quite similar. A detailed analysis further suggested that the contact time giving maximum signal can be used for a quantitative analysis, with only a slight underestimation (ca. 10%) of the fraction of unreacted units, if no correction is made. The amount of unreacted units, typically 0–15%, was found to depend on the polymerization parameters. Conditions favoring mobility, i.e., higher temperature or increased solvent quality, resulted in lower content of residual double bonds.

It is of interest to utilize the double bonds as reactive sites. The mobility should thus be high enough. It was found that bromine can react with the unreacted double bonds. This can in fact be used to determine the content of double bonds, although the obtained values were higher, ca. 2–3%, than those obtained by NMR. However, it is suggested that the mobility is reasonably high. This is also confirmed by measurements of the time constant for carbon relaxation in the rotating frame, $T_{1\rho}(^{13}C)$. The analysis has shown that $T_{1\rho}$ most likely is dominated by spin–lattice processes; i.e., it can be interpreted in terms of molecular dynamics. The values obtained for both C=O and $>C^*=CH_2$ in the unreacted units are about twice that of C=O in reacted units, indicating increased mobility manifested by a higher frequency motion. The reactivity of the remaining double bonds in a radical polymerization with a chiral monomer was also demonstrated.

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