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^{13}C NMR Studies of the Reactions of Cross-Linked Poly(methyl acrylate) Beads with Multifunctional Amines

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ABSTRACT: The kinetics of the functionalization of cross-linked poly(methyl acrylate) beads swollen in dimethylformamide by reactions with various amines was studied by CP/MAS solid-state ^{13}C NMR using the dipolar dephasing technique. In the presence of excess *n*-hexylamine the reaction is first order and the kinetics are unaffected by the diffusion process. However, deviation from simple first-order behavior is observed at high conversions for the reactions with the multifunctional amines 1,6-diaminohexane and tris(2-aminoethyl)amine due to the formation of additional cross-links that hinder the diffusion of these amines within the polymeric beads. The occurrence of the cross-linking reaction is confirmed both by in situ solution ^{13}C NMR studies of the reaction of soluble poly(methyl acrylate) with tris(2-aminoethyl)amine and by ^{15}N NMR studies. The activation energies for the reactions with *n*-hexylamine, 1,6-diaminohexane, and tris(2-aminoethyl)amine are 61, 61, and 65 kJ/mol, respectively, reflecting small differences in polarity of the amines that interact with the reaction intermediates.

Introduction

In recent years polyacrylamides have been studied extensively because of possible pharmaceutical and clinical applications in drug delivery systems and as drug carriers.[1-3] Polyacrylamide can be prepared by polymerization of the corresponding monomers or by the functionalization of polyacrylates by reactions with multifunctional amines. The advantage of the latter method lies in the relative ease with which the polymerizations of acrylates can be controlled so that uniform beads of the desired sizes are obtained.[4-8] However, certain problems have been encountered, the major one being the intramolecular cross-linking that accompanies the functionalization process. The additional cross-links formed during functionalization affect the properties of the functionalized polymer resins and, in the extreme, result in low functionalities and poor swellabilities. A more complete understanding of the features of the kinetics and mechanisms of the these reactions is needed so that conditions can be established such that the formation of the additional cross-links can be minimized.

The development of CP/MAS/DD methods has allowed the suppression of the main solid-state line-broadening mechanisms that result in the poor resolution in solid-state NMR spectra, and these techniques have proven to be useful for the characterization of the cross-linked polymer networks under nondestructive conditions.[9-23] For example, in an investigation of the curing of phenolic resins with formaldehyde under alkaline conditions, Fyfe et al.[10,11] were able to determine the substitution patterns of the phenol rings from their chemical shift values and demonstrate the involvement of the hydroxyl groups of the phenols to produce phenyl benzyl ether bridges. Similarly, Hatfield and Maciel[12] showed that the various methylene bridges that develop during the curing of phenol–formaldehyde resins of the novolak type by hexamethylenetetramine (HMTA) originate from the HMTA. Thus, solid-state NMR has been successfully used in studies of chemical reactions in cross-linked polymer systems, such as the curing of phenolic and epoxy resin,[9-16] cross-linking of elastomers,[17-19] radiation cross-linking,[20,21] and some other polymer network system.[22,23] However, the kinetics of functionalization reactions and related problems, such as the additional cross-linking during the functionalization process, have not been explored to any significant degree.

A previous study of the reaction of ethanolamine with poly(methyl acrylate) demonstrated that, in dimethyl sulfoxide/dichlorobenzene solution, there is an acceleration in rate with increased extent of reaction due to a neighboring group effect.[24] This paper represents an extension of the previous work and reports studies of the kinetics of the reaction of cross-linked poly(methyl acrylate) beads with mono-, di-, and triamines by high-resolution ^{13}C CP/MAS solid-state NMR using a dipolar dephasing technique.

Experimental Section

(A) NMR Spectroscopy. (1) CP/MAS. The ^{13}C high-resolution solid-state NMR spectra were obtained on a Chemagnetics M-100 NMR spectrometer at 25.1 MHz using a Doty Scientific probe under cross-polarization with a magic-angle spinning rate of ~3 kHz. The contact time for cross-polarization was 1 ms and pulse delay times were 3 s. The chemical shifts were referenced to tetramethylsilane (TMS) by setting the chemical shift of the methyl carbon of hexamethylbenzene (HMB) at 17.4 ppm. The data size of all spectra was 1 K, zero-filled to 2 K, and the line intensities were obtained by integration.

The ^{15}N solid-state NMR spectrum was obtained with a Chemagnetics CMX-300 NMR spectrometer operating at a frequency of 30.4 MHz. The sample was packed into a bullet-like zirconia rotor (5-mm diameter), and the MAS was set to be ~4 kHz. Chemical shifts were referenced to ammonia, and the other NMR parameters were as specified above.

(2) CP/MAS with Dipolar Dephasing (DDph). The experiment is similar to a conventional cross-polarization (CP) experiment except for the introduction of a delay, τ, before the application of the proton decoupling pulse.[25] During this period, the transverse magnetization of the ^{13}C nuclei that are strongly coupled to protons, e.g., methylene and methine, dephases due to heteronuclear dipolar interactions in a time that is short compared to the time required for the dephasing of quaternary and methyl carbons. Thus, only signals for the quaternary and methyl carbons remain in the final spectrum.[26] A schematic diagram of the pulse sequence used in the present study is shown in Figure 1,[27,28] where the total dephasing time (τ) is 45 μs. All the NMR conditions were kept identical for the measurements and were the same as those used for the conventional ^{13}C CP/MAS experiments described above.

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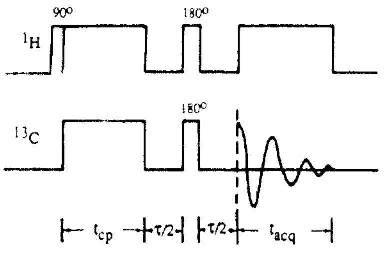


Figure 1. The pulse sequence used for the dipolar dephasing experiment: A 90° ^{1}H spin pulse is followed by a 90° phase shift in the ^{1}H rf to create the spin lock before the ^{13}C rf field, whose magnitude satisfies the Hartmann–Hahn condition, is applied for a time t_{cp}. Both rf fields are turned off again for a period $\tau/2$, a 180° pulse (having the same phase as used during t_{cp}) is applied to each spin system, both rf fields are again turned off for a time $\tau/2$, and finally ^{13}C data acquisition occurs with heteronuclear decoupling for a time t_{acq}.

In DDph NMR, the signal intensity, I, of methoxy and carbonyl groups is determined by[26,29]

$$I = I_0 \exp(-\tau/T_2') \tag{1}$$

where τ is the total dephasing time and T_2' is the dipolar dephasing decay constant which depends on spin diffusion, the strength of the heteronuclear dipolar interactions, molecular motions, relative distances between protons, and MAS rotation speeds.

A basically empirical method, based on the measured relative line intensities, was used to determine the extent of reaction, ξ, from the NMR spectra, according to

$$\xi = 1 - \left(\frac{I_{\mathrm{OCH_3}}}{\sum I_{\mathrm{C=O}}}\right)\left(\frac{I_{\mathrm{C=O}}}{I_{\mathrm{OCH_3}}}\right)_{t=0} \tag{2}$$

where $I_{\mathrm{OCH_3}}$ is the intensity of the resonance for the methoxy carbon, and $\sum I_{\mathrm{C=O}}$ is the sum of the intensities of the peaks for all of the carbonyl carbons. The ratio of the intensities of the carbonyl carbon peaks to that of the methoxy carbon peak of unreacted PMA beads, $(I_{\mathrm{C=O}}/I_{\mathrm{OCH_3}})_{t=0}$, is a correction factor. The validity of eq 2 is based on the assumption that the T_2' values of both the methoxy group and the carbonyl groups do not change as the reaction proceeds. Separate experiments showed that the T_2' of the methoxy group remained virtually unchanged (39 μs) but a small difference in T_2', from 117 to 126 μs, was found for the carbonyl groups as a result of complete functionalization. According to eqs 1 and 2, this would result in an experimental error of ca. 5%.

(3) Solution ^{13}C NMR. The solution ^{13}C NMR spectra were obtained in situ with a Varian XL-300 spectrometer equipped with a 10-mm probe maintained at 110 °C and operating at a frequency of 75.43 MHz. The tip angle was set at 45° and an acquisition time of 0.91 s was used without a time delay. The chemical shifts were referenced to TMS. The reaction was followed for a period of ≥12 h.

(B) Materials and Functionalization. Poly(methyl acrylate) (PMA) beads were prepared by an inverse suspension polymerization method, described in detail previously,[4] using divinylbenzene and triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione as the cross-linking agents and butyl ether and poly(vinyl alcohol) as the pore-forming and stabilization reagents, respectively. All of the chemicals were purchased from Aldrich. The degree of cross-linking was ca. 5% by weight.

Prior to the start of a reaction the PMA beads were swollen in DMF at room temperature overnight. The beads were selected to have diameters in the range of 35–100 μm. The amines were added in a large molar excess (>10 times). The functionalization reactions were performed at different temperatures, thermostated within ±0.2 °C, and efficiently stirred with a mechanical stirrer. At selected times aliquots were taken from the reaction flask and immersed into cold water to terminate the reaction. The beads were immediately separated from the reaction solution by filtration, washed with large amounts of water and methanol, extracted with methanol in a Soxhlet extractor, and finally dried in vacuo at 50 °C for at least 2 days.

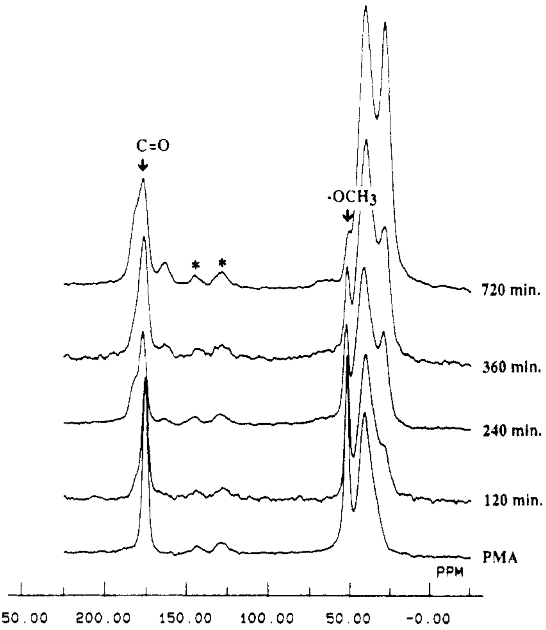


Figure 2. Selected ^{13}C CP/MAS solid-state NMR spectra of PMA reacted with 1,6-diaminohexane for various times at 125 °C. The signals marked with asterisks result from the cross-linking reagent, DVB.

Results and Discussion

A typical set of high-resolution CP/MAS solid-state NMR spectra of PMA beads reacted with 1,6-diaminohexane (DNH) for different periods of time at 125 °C are given in Figure 2. As the reaction time increases, the intensities of the methoxy group signal (δ = 51.7 ppm) decrease and new peaks appear on the high-field side. Concomitantly, the carbonyl peak splits into multiple peaks. This pattern is consistent with the replacement of the ester methoxy groups with *N*-(6-aminohexyl)amide groups by the formation of amide linkages. Because of peak overlap it is difficult to accurately measure the intensities of the methoxy carbon peaks in Figure 2. Attempts to use deconvolution techniques to separate the overlapped lines gave unsatisfactory results.

This problem was resolved by use of solid-state ^{13}C CP/MAS NMR with dipolar decoupling. Figure 3 shows the analogous NMR spectra obtained by use of a total dephasing time of 45 μs. Since the methylene and methine carbon resonances are almost completely attenuated, the methoxy carbon resonance is well separated from the rest so that the intensities can be determined easily by integration. All of the kinetic data were derived from such spectra obtained by the DDph experiments.

In general, the functionalization of PMA by reaction with amines, H_2NR, occurs according to

$$\text{Ⓟ-COOCH}_3 + \text{H}_2\text{NR} \rightarrow \text{Ⓟ-CONHR} + \text{CH}_3\text{OH} \tag{3}$$

Thus, the rate of reaction may be written as

$$\text{rate} = \mathrm{d}[\mathrm{E}]/\mathrm{d}t = k_2[\mathrm{E}][\mathrm{A}] \tag{4}$$

where [E] and [A] represent the concentration of the ester groups of the PMA backbone and the amines, respectively, and k_2 is the reaction rate constant. When the amine is present in large excess, its concentration remains essentially constant during the reaction, and the reaction is first order with respect to the concentration of ester groups; i.e.,

$$\mathrm{d}[\mathrm{E}]/\mathrm{d}t = k_1'[\mathrm{E}] \tag{5}$$

where $k_1' = k_2[\mathrm{A}]$, a pseudo-first-order rate constant. Thus, a plot of $-\ln(1 - \xi)$, where ξ is the extent of reaction, as a

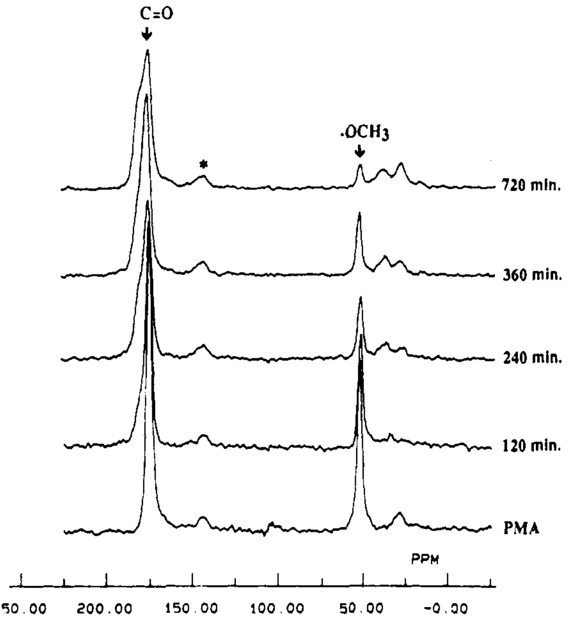


Figure 3. Selected dipolar dephasing ^{13}C NMR spectra of the samples corresponding to those used in obtaining the spectra in Figure 2. The pulse sequence to obtain these spectra is shown in Figure 1. The signal marked with an asterisk results from the cross-linking reagent, DVB.

function of reaction time t should be linear with a slope equal to the rate constant, k_1'.

Because the reaction involves cross-linked polymer beads, albeit porous and highly swollen, the possibility that diffusion of reactants is rate limiting must be taken into consideration. The diffusion process assumes that the concentration of amine is uniform outside the outer boundary of the spherical PMA particle while a concentration gradient of amine exists within. For a bead having a spherical boundary of radius r, hence a surface area of $4\pi r^2$, Fick's first law of diffusion[31] gives

$$J_A = 4\pi r^2 D_A (dC_A/dr) \tag{6}$$

where J_A is the diffusion flux, C_A is the local concentration of amine, and D_A is the diffusion constant. Assuming that D_A is a constant, integration with the boundary condition that $C_A = C_A°$, the bulk concentration, at $r = \infty$ gives

$$C_A = -(J_A/4\pi D_A r) + C_A° \tag{7}$$

At a certain critical distance r_{cd}, where $C_A = C_A^*$, the rate of removal of A by reaction with ester groups is $k_2 C_A^*$. For steady-state conditions the rate is equal to the diffusion flux, J_A, so that

$$C_A^* = C_A°/(1 + k_2/4\pi D_A r_{cd}) \tag{8}$$

Then the rate of reaction at r_{cd} is given by

$$(\text{rate})_{cd} = k_2[E]C_A^* = k_2[E][A]/(1 + k_2/4\pi D_A r_{cd}) = k_{app}[E][A] \tag{9}$$

where

$$k_{app} = k_2/(1 + k_2/4\pi D_A r_{cd}) \tag{10}$$

Two extreme cases exist: (i) when $k_2 \gg 4\pi D_A r_{cd}$, then $k_{app} = 4\pi D_A r_{cd}$, which represents the case of a fully diffusion-controlled reaction; (ii) when $4\pi D_A r_{cd} \gg k_2$, then $k_{app} = k_2$, which represents the case where there is no diffusion control and the reaction rate is controlled by the rate of the chemical reaction.

The data for the functionalization of PMA by the reaction with n-hexylamine (HAN) at 125 °C fit well to a plot of $-\ln(1 - \xi)$ as a function of reaction time, even for very high conversions (Figure 4). The slopes yield $k_{app} = k_2 = 2.3 \times 10^{-4}$ and 2.4×10^{-4} L·mol^{-1}·min^{-1} when the concentrations of HAN are 3.1 and 6.2 mol/L, respectively. Good linearity in the first-order plots is also obtained at lower reaction temperatures (Figure 5), and the derived values of k_2 (Table I) yield an activation energy of 65 kJ/mol (Table II). Thus, in the presence of a large molar excess of HAN the data for the functionalization of PMA show a good fit to pseudo-first-order kinetics, indicating rapid diffusion of HAN within the cross-linked PMA beads so that $4\pi r^2 D_A r_{cd} \gg k_2$.

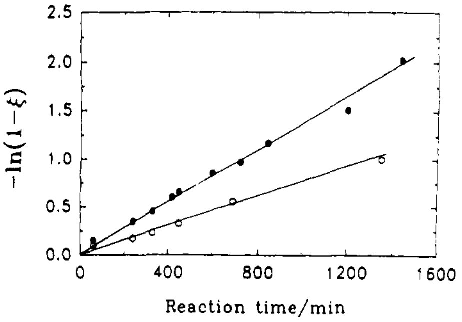


Figure 4. Dependence of $-\ln(1 - \xi)$ on the time of reaction of PMA with different concentrations of n-hexylamine (HAN) in DMF at 125 °C: (●) 6.2 and (○) 3.1 mol/L.

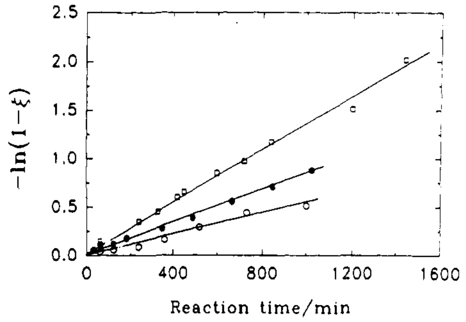


Figure 5. Dependence of $-\ln(1 - \xi)$ on the time of reaction of PMA with n-hexylamine (HAN) at 6.2 mol/L in DMF at different temperatures: (□) 125, (●) 118, and (○) 110 °C.

Table I
Rate Constants for the Functionalization of PMA by Reaction with Different Amines at Various Temperatures

reaction	temp (K)	concn (mol/L)	$k_1' \times 10^4$ (min^{-1})	$k_2 \times 10^4$ (L·mol^{-1}·min^{-1})
PMA-HAN	383	6.20	7.00	1.13
	391	6.20	8.37	1.35
	398	6.20	15.2	4.06
PMA-DNH	388	3.10	6.96	2.25
	398	3.10	14.9	5.29
	408	3.10	21.2	6.84
PMA-TREN	353	3.10	1.18	0.38
	378	3.10	6.97	2.25
	398	3.10	11.7	3.61

Table II
Activation Parameters for the Reactions of PMA with Amines

reaction	ln A	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)	ΔS^* (J·mol^{-1}·K^{-1})
PMA-HAN	15.2	64.6	62.2	110	-160
PMA-DNH	15.5	64.5	62.0	109	-159
PMA-TREN	14.0	60.7	58.2	109	-171

It should be kept in mind that the presence of excess HAN may influence the functionalization process. As the reaction proceeds, the functionalized polymer becomes more compatible with HAN so that polymer–solvent contacts are improved. As a result, the chains of the functionalized polymer tend to expand, and this additional swelling favors the diffusion.

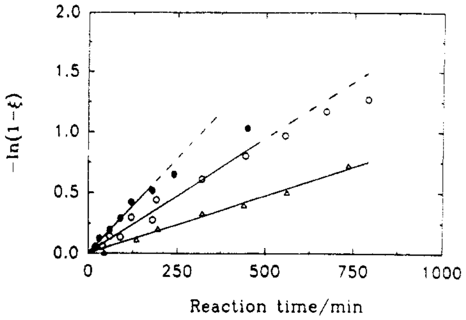


Figure 6. Dependence of $-\ln(1-\xi)$ on the time of reaction of PMA with 1,6-diaminohexane (DNH) at 3.1 mol/L in DMF at different temperatures: (●) 135, (○) 125, and (△) 105 °C.

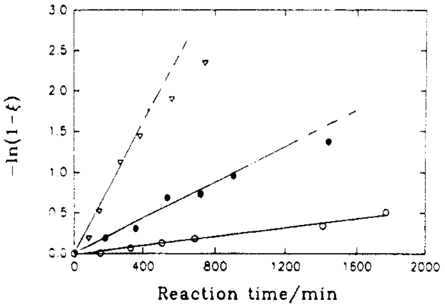


Figure 7. Dependence of $-\ln(1-\xi)$ on the time of reaction of PMA with TREN at 3.1 mol/L in DMF at different temperatures: (▽) 125, (●) 105, and (○) 80 °C.

The data for the reaction of PMA with 1,6-diaminohexane, shown in Figure 6, begin to show deviation from first-order kinetics as the extent of reaction increases. The values of k_2 (Table I), derived from the initial slopes, are in good accord with those for the reaction with HAN and yield similar activation parameters (Table II). In the determination of rate constants the concentration of amino groups was assumed to be twice the molar concentration of DNH.

Since each DNH molecule is a diamine, the second amino group is still available for a reaction that results in intramolecular cross-linking, and consequently the diffusion constant, D_A, is dependent on the extent of conversion. At the low conversions the extra cross-linking is minimal so that the diffusion of DNH is not affected significantly. However, as more intramolecular cross-links are formed, D_A changes to the point where the requirement that $4\pi r^2 D_A r_{cd} \gg k_2$ is no longer fulfilled, and the observed deviation from the overall pseudo-first-order kinetics is expected.

The cross-linking reaction is kinetically possible because, although the apparent concentration of the attached amino groups within the beads is low compared with the bulk amine concentration, the effective concentration may be considerably higher due to the entropic effect.[32] The probability of the reaction of attached amino groups is related to the flexibility of the polymer chains. The fact that the T_g of PMA is 2 °C suggests considerable flexibility of the main chain of the polymer so that the interaction of the ester carbonyl groups with the residual amino groups is possible.

As expected, additional cross-linking also occurs during the functionalization of PMA beads by the reaction with the trifunctional amine tris(2-aminoethyl)amine (TREN), as indicated by a downward curvature toward the time axis at high conversions in the plot of the kinetic data (Figure 7). At any given temperature the rate constant, k_2, for the reaction of PMA with TREN is somewhat higher than those for the reactions with HAN and DNH (Table I) while the activation energy is somewhat lower (Table II). After the initial reaction, two amino groups of TREN remain available for further reaction with sterically accessible ester groups.

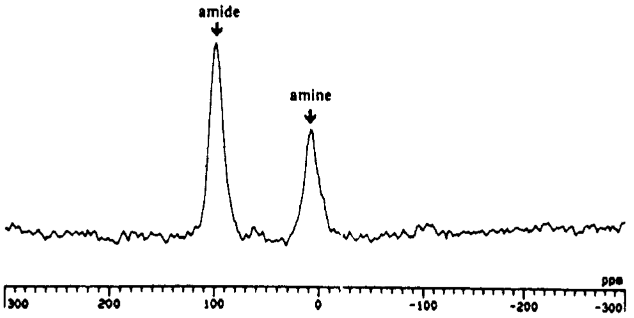


Figure 8. Solid-state CP/MAS ^{15}N NMR of PMA functionalized by reaction with TREN at 125 °C for 12 h.

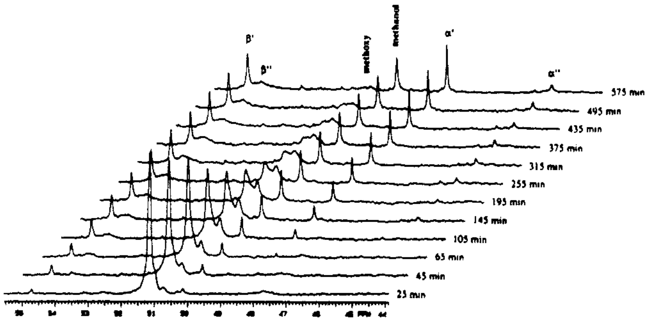
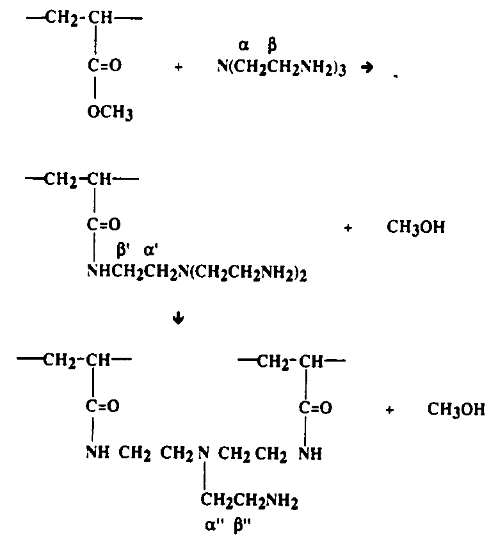


Figure 9. Stack plot of a selected portion of the solution ^{13}C NMR spectra of functionalized PMA which has been allowed to react with TREN in DMSO for various times.

Because the chemical shifts of the reacted groups are not resolved from those for the unreacted groups in the solid-state NMR spectra, direct evidence for the intramolecular cross-linking is not available. However, the CP/MAS ^{15}N NMR spectrum of PMA functionalized by the reaction with TREN (Figure 8) shows that the intensity ratio of amino ^{15}N to that of amide ^{15}N is much less than the theoretical value, 3:1, which is consistent with the extra cross-linking.

To consider this matter further, in situ ^{13}C NMR studies were made of the functionalization of an *un-cross-linked* PMA by reaction with TREN in DMSO at 110 °C. As expected, the intensity of the peak for the methoxy group (51.4 ppm) decreases with reaction time (Figure 9). Concurrently, this peak shows splitting owing to the change in the distribution of triads. Together with this, peaks assigned to $C_{\alpha'}$ and $C_{\beta'}$ in 1 appear at 54.8 and 48.6 ppm, respectively. The chemical shifts corresponding to carbons on the unreacted side chains, which are not affected significantly by the substitution, overlap with the corresponding resonances of excess TREN in solution (C_α, 58.0 ppm, and C_β, 39.8 ppm, in DMSO-d_6 (not shown in Figure 9)). As the reaction proceeds, the CH_3OH carbon signal at 50.3 ppm increases and small, but noticeable, peaks, assigned to $C_{\alpha''}$ and $C_{\beta''}$ in 1, appear at 45.4 and 54.2 ppm, respectively. The intensities of these peaks, which first appear at very low conversions, increase with the increase in conversion but are not directly proportional to those of $C_{\alpha'}$ and $C_{\beta'}$. This is in agreement with the occurrence of inter- and/or intramolecular cross-linking as part of the functionalization.

It is evident here that the residual amino groups of reacted TREN, although in small amount compared with that of the TREN in the bulk solution, are able to undergo cross-linking reactions at a rate that is competitive with that of the major reaction. At the low conversions, the concentration of ester groups is high so that the cross-linking reaction of the amino groups of reacted TREN is



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relatively fast. However, as the reaction proceeds, the concentration of ester groups diminishes so that the rate of cross-linking decreases. Consequently, the intensities of $C_{\alpha''}$ and $C_{\beta''}$ are not directly proportional to those of $C_{\alpha'}$ and $C_{\beta'}$.

Separate experiments showed that, when the ratio of initial concentration of TREN to PMA is decreased from 3 to 1, the intensities of both $C_{\alpha''}$ and $C_{\beta''}$ increase and all of the peaks become broader, in accord with additional cross-linking. This was confirmed by the observation that when the initial molar ratio of TREN to the monomer units of PMA was 3, a very viscous, but movable, "solution" was obtained after complete reaction. By comparison, a nonmovable gel was obtained when the ratio was 1. As expected, the increase in the concentration of TREN favors the major functionalization step while the cross-linking reactions are able to compete more effectively at lower amine concentrations.

The activation energies for the functionalization reactions of PMA with HAN and DNH are essentially equal while that for reaction with TREN is somewhat smaller (Table II). The same trend is obtained in enthalpies of activation (Table II) computed by use of

$$\Delta H^{\ddagger} = E_a - RT \qquad (11)$$

It is well known[33] that the substitution of an ester by an amino group involves a partially charged, tetrahedral reaction intermediate that is affected by polarity of the solvent. Better solvation of the intermediate should occur for the reaction with TREN, which has a higher polarity, than with either HAN or DNH. As a consequence, the transition state of the reaction with TREN is expected to have the lowest energy barrier.

Additional evidence for increased solvation in the PMA–TREN system is seen in the entropies of activation, $\Delta S^{\circ\ddagger}$, as calculated from

$$A/60 = e(kT/h)\exp(\Delta S^{\circ\ddagger}/R) \qquad (12)$$

where e is a constant, A is the preexponential factor, k is the Boltzmann constant, and h is Planck's constant. The $\Delta S^{\circ\ddagger}$ for the PMA–TREN reaction is the most negative (Table II), while those for the PMA–HAN and PMA–DNH reactions are more or less equal. The large negative values in $\Delta S^{\circ\ddagger}$ for all of these reactions reflect a charge separation for the reaction intermediate. Because differences in the enthalpic effect are essentially canceled by the entropic effect, the $\Delta G^{\circ\ddagger}$ for these three systems are the same.

Conclusions

Additional cross-linking during functionalization of cross-linked poly(methyl acrylate) with multifunctional amines was determined through kinetic studies and through the corresponding linear polymer functionalization by means of CP/MAS solid-state NMR and in situ solution NMR. The formation of the additional cross-links hampers the functionalization reaction rates by affecting the diffusion of amines in the polymeric beads. Experimental results suggest that the functionalization of PMA with multifunctional amines is best done in the presence of excess amine to avoid additional cross-linking and, hence, obtain polymer with higher functionality.

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