

# Characterization and Application of Crosslinkers for Polyurethane Aqueous Systems: Isopropylidene Malonate-Blocked Isocyanurate

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## SYNOPSIS

An adduct of hexamethylene isocyanurate and isopropylidene malonate was prepared and tested as a crosslinker in a one-pack water-borne polyurethane system. It was characterized by FTIR, NMR, and SEC; the blocking and curing courses were followed by FTIR and DSC. The crosslinker was a mixture of various oligomers having mainly amide-type linkages. The cure analysis showed that cleavage of the malonate ring started at around 110°C and was followed by the formation of ester-type products. After 30 min of heating at 130°C the insoluble part of crosslinked polyurethane films exceeded 80%. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

According to the increased interest in the replacing of solvent-borne with water-borne polymer systems, due to environmental reasons, several polyurethane (PU) ionomers as well as monomeric and oligomeric ionomer crosslinkers have been synthesized.<sup>1–5</sup> The one-pack PU water dispersions containing blocked isocyanate compounds as latent crosslinkers are of special importance to the coatings.

A great number of blocked isocyanates were reviewed by Wicks<sup>6,7</sup> and Potter et al.<sup>8,9</sup> By blocking the isocyanates with some nucleophilic reactants, adducts with relatively weak bonds, stable at ambient temperature, are formed. At elevated temperatures the isocyanate ( $\text{—NCO}$ ) groups regenerate and react with stronger nucleophiles to give thermally more stable bonds. These adducts are effective crosslinkers when used in thermal curing and, generally, films with improved mechanical and chemical properties are obtained. However, in the case of reactive-methylene blocking agents, the mechanism of deblocking and crosslinking is more complicated; instead of the simple regeneration of  $\text{—NCO}$  groups, some complex reactions can take place, including the formation of amides, esters, ketenes, and

other products.<sup>10,11</sup> The blocking and curing behavior of this type of blocked compounds has not been examined to a larger extent.

Our previous work on one-pack water-borne PU systems has studied some blocked PU ionomers and ionomeric blocked polyisocyanate crosslinkers, using butanonoxime (BOX) as a blocking agent.<sup>12,13</sup> For further investigation in the field of blocked isocyanates, a reactive-methylene cyclic dicarbonyl compound isopropylidene malonate (known as Meldrum's acid—MA) was chosen because of its triple function. Namely, it enables the blocking of  $\text{—NCO}$  groups, solubility in water, and crosslinking with compounds containing hydroxyl groups.<sup>14</sup> In the case of MA-blocked triisocyanates, all three  $\text{—NCO}$  groups are available for blocking and consequently for crosslinking; while with BOX, only two  $\text{—NCO}$  groups can be blocked since the third one is used for the reaction with a hydrophilic compound to provide water solubility. Therefore, MA-blocked adducts were expected to be better crosslinkers than BOX-blocked adducts.

The synthesized crosslinkers were characterized by infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, and by size exclusion chromatography (SEC). The blocking reaction was followed by using FTIR spectroscopy, while the crosslinking reaction with hydroxy functional compounds was followed by FTIR and differential scanning cal-

**Table I** Composition–Properties Correlations of the Blocked Isocyanates

Sample	Equiv. Ratio DDA : MA : TEA	Conversion After 3 Hours (%)	Solubility in Water	Solubility of Dried Adducts in THF
1	1 : 1 : 1.5	100	clear solution	soluble
2	1 : 1 : 1	92	colloid solution	soluble
3	1 : 1 : 0.5	76	dispersion with sediment	partly soluble
4	1 : 1 : 0.25	40	dispersion with sediment	partly soluble

orimetry (DSC). The crosslinking efficiency of the blocked adduct was estimated by THF extraction of the crosslinked ionic PU resin.

## EXPERIMENTAL

### Materials

1,3,5-tris(isocyanatohexamethylene)isocyanurate, desmodur DA (DDA, Bayer), 2,2-dimethyl-1,3-dioxane-4,6-dione, synonym Meldrum's acid (MA, Aldrich), and polyethylene glycols (PEG200 and PEG400,  $M_n = 200$  and  $M_n = 400$ , Riedel-de Haën) were used as received. Triethylamine (TEA, Merck) and tetrahydrofuran (THF, Merck) were dried by standard procedures.

### Synthesis

Blocked isocyanate adducts were prepared by a dropwise addition of TEA to a mixture of DDA and MA in THF solution with stirring at room temperature; after adding the whole amount of TEA, the temperature was raised to 50°C.<sup>14</sup> The blocking reaction was controlled by scanning the FTIR spectra. After the reaction completion, the adducts can be

**Table II** The Gel Fraction of the PU Films Crosslinked with Sample 2 in Table I

Mole Ratio MA : OH	Temperature (°C)	Time (min)	Gel Fraction (%)
0.1 : 1	130	60	25.0
0.5 : 1	110	60	35.2
0.5 : 1	130	30	83.6
0.5 : 1	130	60	84.2
1.0 : 1	110	60	43.3
1.0 : 1	130	60	80.6
1.5 : 1	130	60	81.0
2.0 : 1	130	60	82.4

dissolved or dispersed in water. The equivalent ratio between DDA and MA was 1 : 1, while the share of TEA varied from 0.25 to 1.5. The adduct with an equivalent ratio DDA : MA : TEA = 1 : 1 : 1 (Sample 2, Table I) was taken for further examination. For its easier characterization, the model adduct of MA with TEA (1 : 1 equivalent ratio) was prepared.

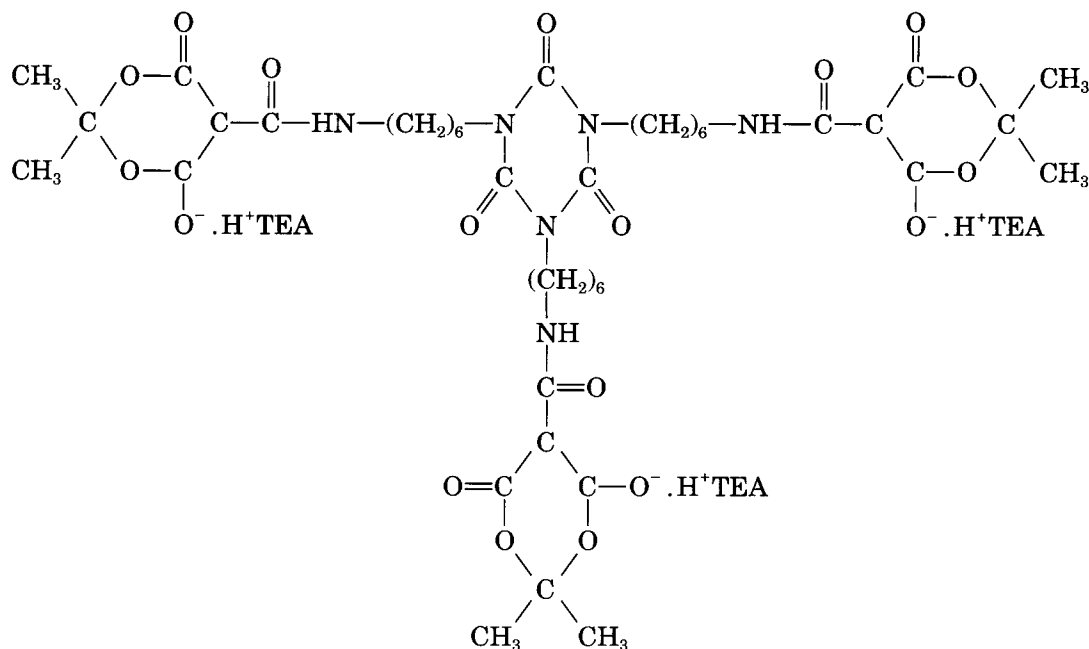
For cure analysis, the crosslinker was mixed with polyethylene glycol or with anionic PU dispersion containing 0.1 mmol g<sup>-1</sup> of free —OH groups. The mole ratio between —NCO and —OH groups was 1 : 1. Before analysis, the samples were dried in a vacuum drier at 50°C for 24 hours.

### Methods

FTIR spectra were recorded on a Perkin–Elmer 1725X spectrometer. The measurements at temperatures from 25° to 230°C were performed by using a variable temperature cell connected with a temperature controller. For NMR measurements, a Varian VXR 300 spectrometer at a frequency of 300 MHz for <sup>1</sup>H and 75.4 MHz for <sup>13</sup>C was used under the following conditions: pulse angle 45° and 60°, pulse delay 2s and 1s, respectively. The chemical shifts were quoted to TMS. The molar mass distribution was measured by a Perkin Elmer liquid chromatograph using an LC-30 RI detector, PL gel columns 500 and 100 Å, and THF as eluent. DSC measurements were performed on a Perkin Elmer DSC-7 by heating the samples in the temperature range from 25° to 270°C with a rate of 5°C/min. The films of the PU dispersions containing different amounts of the crosslinker were crosslinked by heating at 110° or 130°C. The insoluble part (gel fraction) of the crosslinked PU films was determined by THF extraction in a Soxhlet apparatus for 6 hours.

## RESULTS AND DISCUSSION

Table I shows the correlation between the composition of the MA-blocked adducts and conversion



Scheme 1

after 3 hours, solubility in water, and solubility of the dried (at room temperature) adducts in THF.

The results show that the extent of reaction exceeded 90% only if the amount of TEA equaled or exceeded that of MA. When the amount of TEA was smaller (Samples 3 and 4, Table I), the solubility or dispersibility of the adducts in water was poor. After drying at room temperature, these samples were partially insoluble in THF as well. That was attributed to some crosslinking reactions of the MA component. It was found, namely, that MA degraded and/or reacted to some extent in organic solvents to give different products.<sup>15</sup> According to our results, the addition of an equivalent amount of TEA had a stabilizing effect on MA solutions.

The structure of the triblocked isocyanate (Sample 2 in Table II) used as a crosslinker in our further investigation is presented in Scheme 1.

Some information on the composition of the crosslinker (Sample 2) was obtained by comparing its SEC curve (a) with that of DDA (b) (Fig. 1). The highest peak ( $M_{\text{peak}} = 602$ ) in curve (b) belongs to DDA, while the highest peak ( $M_{\text{peak}} = 1141$ ) in curve (a) corresponds to the crosslinker given in Scheme 1. Some higher oligomers were ascribed to blocked products of the oligomers already present in DDA. Additionally, a small amount of MA component might have decomposed during the synthesis, thus secondary reactions could have taken place to a small extent. When TEA was not added during

the synthesis, some gelation and gaseous products were observed. So far, these products have not been examined.

The course of the blocking reaction was followed by a decrease of  $\text{—NCO}$  absorbance band at 2276

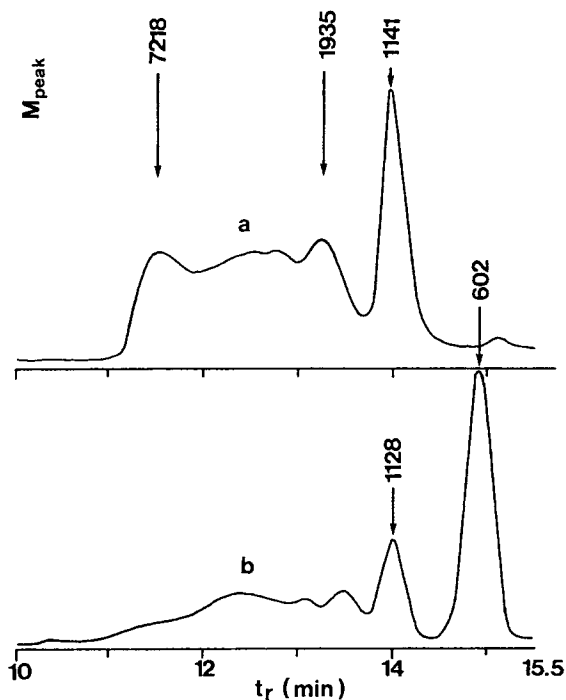
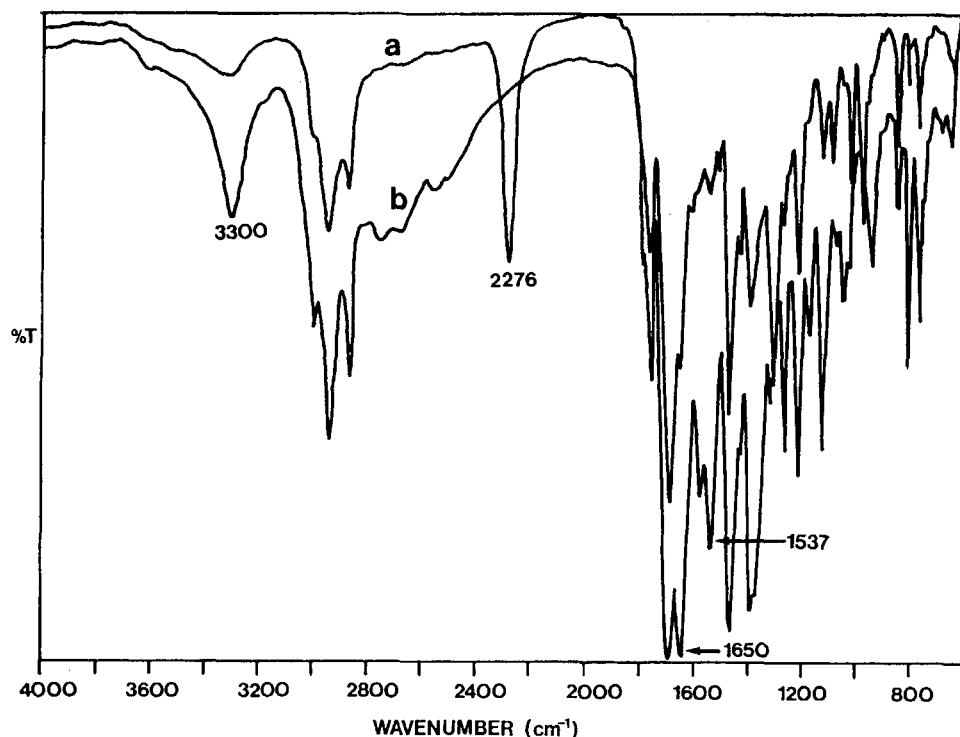


Figure 1 SEC curves of the crosslinker (a) and of DDA (b).

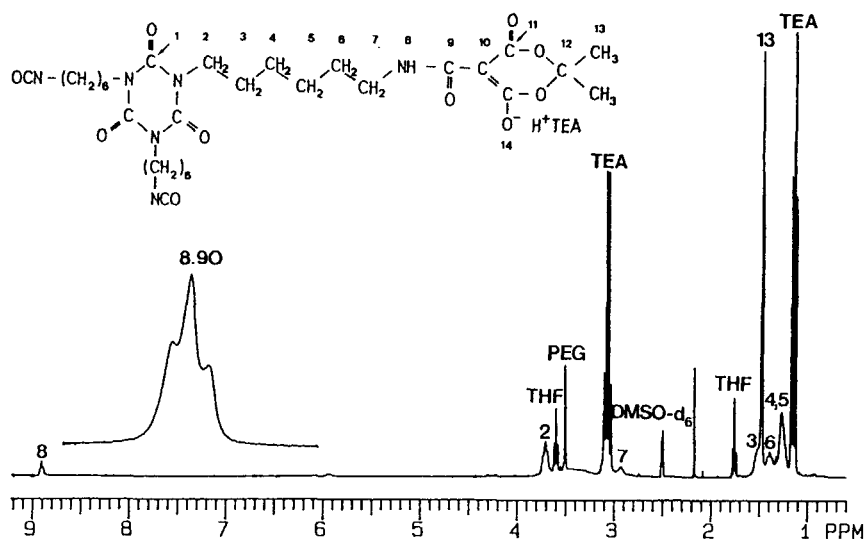


**Figure 2** FTIR spectra of the reaction mixture DDA : MA : TEA = 1 : 1 : 1 before heating (a) and at the end of the blocking reaction (b).

$\text{cm}^{-1}$  in the FTIR spectra. The spectra presented in Figure 2 were taken after adding the whole amount of TEA (a) and at the end of the reaction (b). An amide-type structure was supposed to be formed due to the appearance and growth of an amide N—H stretching vibration band at  $3300\text{ cm}^{-1}$  and an amide II band at  $1537\text{ cm}^{-1}$  (N—H deformation and

C—N stretching vibrations). The amide I band (C=O stretching) at  $1650\text{ cm}^{-1}$  was partly overlapped by the C=O bands of isocyanurate ring and MA C=O groups in the region of  $1700$  to  $1640\text{ cm}^{-1}$ .

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of the crosslinker (Figs. 3 and 4) confirmed the formation of an amide structure. The signal at  $8.90\text{ ppm}$  belonged to hy-



**Figure 3**  $^1\text{H}$ -NMR spectrum of the crosslinker.

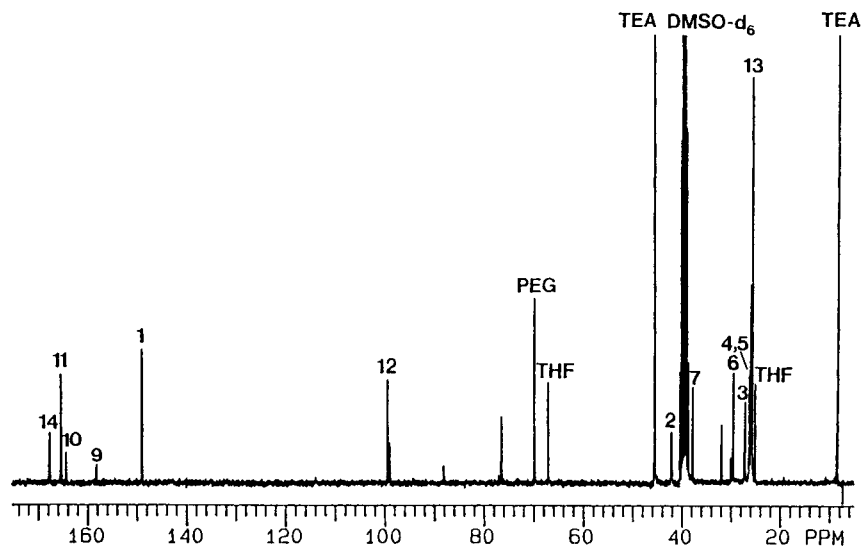


Figure 4  $^{13}\text{C}$ -NMR spectrum of the crosslinker.

drogen atoms and the signal at 158.2 ppm to carbon atoms of the amide groups. The signals at 165.2 and at 167.6 ppm were ascribed to C atoms in keto and ionic forms of the MA component, whereas the signal at 164.3 ppm was ascribed to the C atom of MA attached to the amide group. However, some additional signals (e.g.,  $^1\text{H}$  signal of amine  $-\text{NH}_2$  group

at 5.95 ppm) indicated that side reactions had also taken place. The assignment of other resonances is given in Figures 3 and 4. The signals at 3.5 ppm and 69.8 ppm, respectively, belong to polyethylene glycol (PEG) in DDA, added in a small amount (0.2 mol %) presumably to suppress its crystallization during storage.<sup>16</sup>

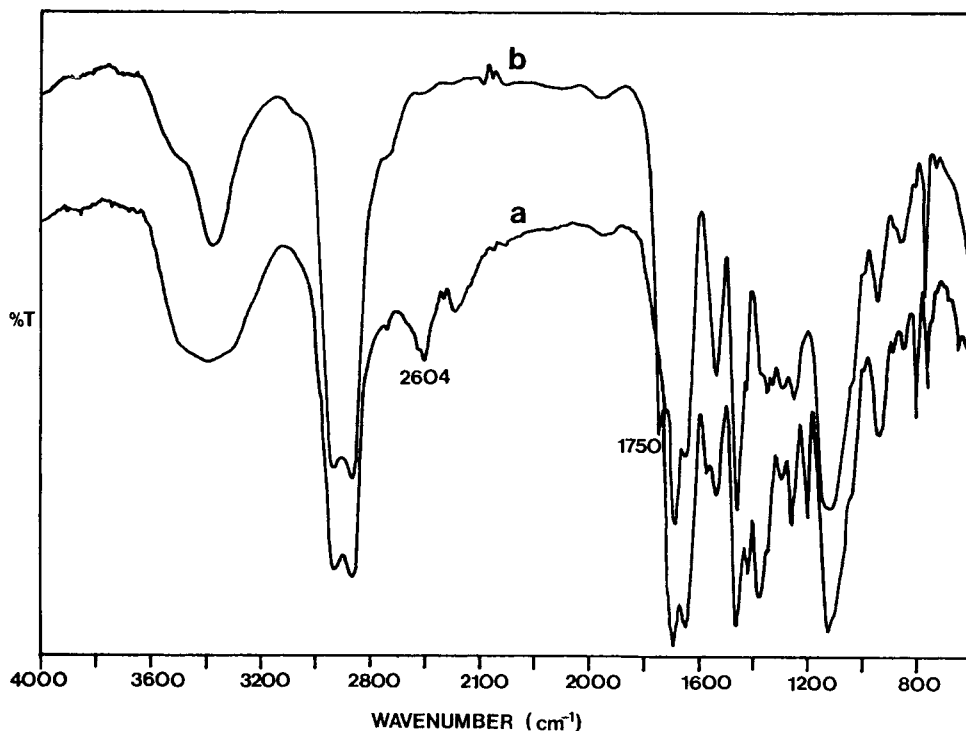


Figure 5 FTIR spectra of the mixture of the crosslinker and PEG400 before heating (a) and after heating at 130°C for 30 min (b).



and, further, the presence of the amide N—H, amide I, and amide II bands (at 3306, 1650, and 1537  $\text{cm}^{-1}$ , respectively). The new band at 1750  $\text{cm}^{-1}$  was attributed to the aliphatic ester C=O group vibrations of malonamic ester compounds (Scheme 2). The broad band at 2604  $\text{cm}^{-1}$  in Figure 5(a) was ascribed to the strong H-bonding between —OH groups of PEG400 and C=O groups of the crosslinker. The spectra of the heated films showed no evidence of ketene intermediates which were observed in some malonate-blocked isocyanates (band in the region of about 2090  $\text{cm}^{-1}$ ).<sup>17</sup>

DSC curves of the reaction mixtures of the crosslinker with polyethylene glycols or with PU ionomer (Figure 6) showed an exothermic reaction with a maximum at around 145°C, which was attributed to the complex crosslinking reaction (cleavage of the MA ring followed by esterification) presented in Scheme 2. The kinetics of the overall reaction for the mixture of the crosslinker with PEG400 was calculated; the enthalpy was found to be 43 kJ per mole of —OH groups, the activation energy 115 kJ per mole of —OH groups, and the overall reaction order 1.5.

The crosslinker efficiency at 110°C and 130°C was estimated by determining the gel fraction in crosslinked PU films after 60 or 30 min of curing (Table II). The gel fraction over 80% was obtained with the samples having 0.5 mole or more of the MA component (calculated per mole of —OH groups in PU ionomer) heated at 130°C.

These results are very similar to the results obtained with the BOX-blocked ionic crosslinker.<sup>13</sup> The efficiency of the MA-blocked crosslinker was lower than expected; this was ascribed to the partial degradation of MA during the synthesis (cleavage of its ring, splitting of some volatile products), resulting in reduced functionality of the crosslinker.

## CONCLUSIONS

The structure of the crosslinker obtained by blocking hexamethylene isocyanurate with isopropylidene malonate (MA) in the presence of triethylamine was investigated by FTIR, NMR, and SEC techniques. The crosslinker was found to be a mixture of oligo-

mers having amide linkages. The addition of at least an equivalent amount of TEA with regard to the blocking agent was needed to stabilize MA and to ensure the water solubility of the crosslinker.

Crosslinking reactions include the splitting of the MA ring and the reaction with —OH functional compounds, giving aliphatic ester-type products. By adding the crosslinker to a PU ionomer resin, stable one-pack water-borne PU dispersions were obtained. Efficient crosslinking was achieved at 130°C; the insoluble part of crosslinked films exceeded 80%.

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