

An NMR Study of the Dissociation of *N,N'*-(2-propyloximino)-4,4'-Methylenebis(phenylcarbamate) and Its Crosslinking of Polymers Containing Labile Hydrogens. II

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Synopsis

Nuclear magnetic resonance spectroscopy has been used to study the dissociation and reaction of *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate), as a crosslinking agent for polymers containing labile hydrogens. The crosslinking of poly(acrylic acid), polyacrylamide, and poly(vinyl alcohol) was found to result upon heating each to 150°C for 10 min with this component at 2–10 wt %.

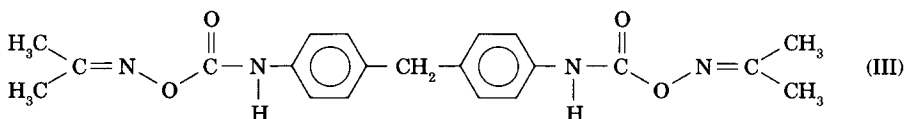
INTRODUCTION

Polymers with labile hydrogens can react with 4,4'-methylenebis(phenylisocyanate) (MDI) to form crosslinked polymers. The isocyanate group can be effectively "blocked," however, by various hydroxyl containing compounds such as phenols, acids, and oximes.¹ The blocked diisocyanate can consequently be introduced into a polymer system, later to be activated as a crosslinking agent. This allows for polymer manipulation or orientation to a preferred state prior to crosslinking. By then heating above the dissociation temperature (T_d), of the blocked diisocyanate, the active isocyanate ($-\text{N}=\text{C}=\text{O}$) group is regenerated and crosslinking can occur.

BACKGROUND

N,N'-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate) (III) has been synthesized, characterized, and used as a post-polymerization crosslinking agent (PPCA), in the modification of elastic polyurethane fibers.²⁻⁴ As a consequence, the objective of this work is twofold. We first examine the dissociation upon heating of III to acetone oxime (I) and MDI (II) and, secondly, observe the reaction of III with three polymers with labile hydrogens.

Both Parker¹ and Sun et al.²⁻⁴ have used similar routes to synthesize (III). The structure has been shown by ¹H- and ¹³C-NMR to be⁵:



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Parker determined the melting point (T_m) and dissociation temperature (T_d) to both be $\sim 128^\circ\text{C}$. He also noted that the transition varied with the test method. By observing the regeneration of diisocyanate by infrared spectroscopy (IR), a T_d of 112°C was noted. Parker attributed this difference to the OH containing solvents used in the determination.

Sun and co-workers have characterized (III) by DSC, IR, and elemental analysis. They report a T_m of 123°C and a prominent decomposition, T_d , at $\sim 140^\circ\text{C}$. The reaction of (III) with a block copolymer of polyurethane and an aliphatic polyester was investigated by Choli et al.⁶ using solid state NMR.

EXPERIMENTAL

Measurements. Carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectra were recorded on a Varian CFT-20 Variable Temperature Spectrometer at 20 MHz. The spectra were collected using both $5\ \mu\text{s}(30^\circ)$ and $15\ \mu\text{s}(90^\circ)$ pulses with pulse delay times of 1.023 and 10.023 s. The spectral width was 4000 Hz (200 ppm) with a peak resolution of 0.2 Hz. Operating probe temperatures were controlled between 35°C and 160°C (-1.0°C). Proton noise decoupling, off-resonance decoupling, and gated (non-NOE) decoupling techniques were used when necessary.

Proton NMR (^1H -NMR) spectra were recorded on a 90 Hz Perkin-Elmer R-32 Spectrometer equipped with a variable temperature probe. The spectral width was scanned over 1800 Hz (20 ppm) with a peak resolution of 0.3 Hz. NMR experiments were carried out using 2–5% (w/v) polymer samples dissolved in dimethyl sulfoxide (DMSO d_6) with hexamethyl disiloxane (HMDS) as an internal standard.

Thermoanalysis. A Perkin-Elmer DSC-2 Differential Scanning Calorimeter with TADS was used to observe the melting (T_m) and dissociation (T_d) temperatures at a programmed heating rate of $10^\circ\text{C}/\text{min}$.

The thermodegradation was carried out on a Perkin-Elmer TGS-2 thermogravimetric Analyzer under a nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$.

MATERIALS

N,N'-(2-propyloximino)-4,4'-methylene bis(phenylcarbamate) was prepared according to a prior method.^{2,4}

Polyacrylamide. Ten grams of acrylamide (99+%, Aldrich Chemical Co.) was dissolved in 50 mL double-distilled H_2O . To the solution was added 50 mg Ammonium Persulfate (AR, Mallinckrodt) and 25 mg *N,N,N,N*-tetramethylethylene diamine (AR, Mallinckrodt). The polymer was formed while holding the solution for 1 h at 25°C . The polymer gel obtained was rinsed with ice distilled water and dried over P_2O_5 in a vacuum desiccator for several days.

Poly(acrylic acid). Aldrich Chemical Co., mol. wt. 250,000.

Poly(vinyl alcohol). Aldrich Chemical Co., mol. wt. 16,000, 98% hydrolyzed.

RESULTS AND DISCUSSION

Thermoanalysis. Differential scanning calorimetry (DSC) on III showed two endotherms, one at 123°C and the other at 155°C. The peak intensities of both peaks were somewhat less than expected for either the melting with dissociation (123°C) or the boiling of the acetone oxime. Thermogravimetric analysis (TGA) in Figure 1 shows a slow decomposition starting at 123°C to approximately 50% of its initial weight. A reduction to 63% would be expected upon volatilization of acetone oxime (bp 135°C). Apparently, above 123°C, reaction occurs until the acetone oxime is driven off, shifting the equilibrium to yield the unblocked MDI.

For a more detailed picture of the reaction, carbon-13 (^{13}C) and proton (^1H) nuclear magnetic resonance (NMR) spectroscopy was used to observe the effects on heating of (III). Both ^{13}C - and ^1H -NMR results showed no change in the blocked diisocyanate up to 123°C. Above 123°C, however, several resonances appeared to confirm the onset of dissociation of III.

^{13}C -NMR. Figure 2 shows the ^{13}C spectra at 120°C (a) and 150°C (b) with chemical shift assignments established from previous work.⁵ It can be seen that the carbonyl (III-6) at 161.8 ppm is no longer present at 150°C. A new signal at 152.5 ppm, however, suggests that a urethane type of carbonyl was formed, while phenyl carbons III-2 and 3 were observed. Their bond intensity was due to the increased nuclear overhauser effect (NOE) they exhibit over the other carbons in III. The phenyl region (110–140 ppm) becomes more complex; however, no peak could be discerned for the $-\text{N}=\text{C}=\text{O}$ group expected in the regeneration of MDI.

The peak at 14.4 ppm was found to correspond to the CH_3 (I-c') of the acetone oxime (*cis* to oxygen) while the expected shift for the CH_3 (I-a') *trans* to the oxygen (21.5 ppm) was overlapped by the analogous carbon (III-a) of the blocked diisocyanate at 21.2 ppm. The nonprotonated carbon I-b was observed at 155.3 ppm.

From experiments at various temperatures and times, the extent of dissociation was calculated. Using gated decoupling the ^{13}C resonances were quantitatively observed for the regeneration of acetone oxime. Figure 3 shows the change with time of the peak areas for the methyl groups. After heating the sample at 150°C for 2, 10, and 60 min the "unblocking" had proceeded by ~15, ~50 and ~98%, respectively.

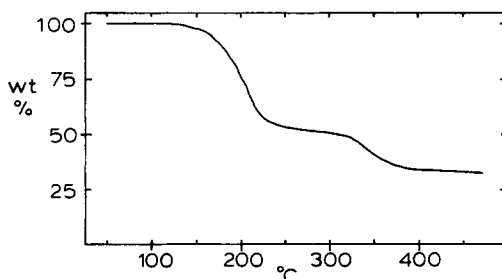


Fig. 1. TGA thermograms of the decomposition of *N,N*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate).

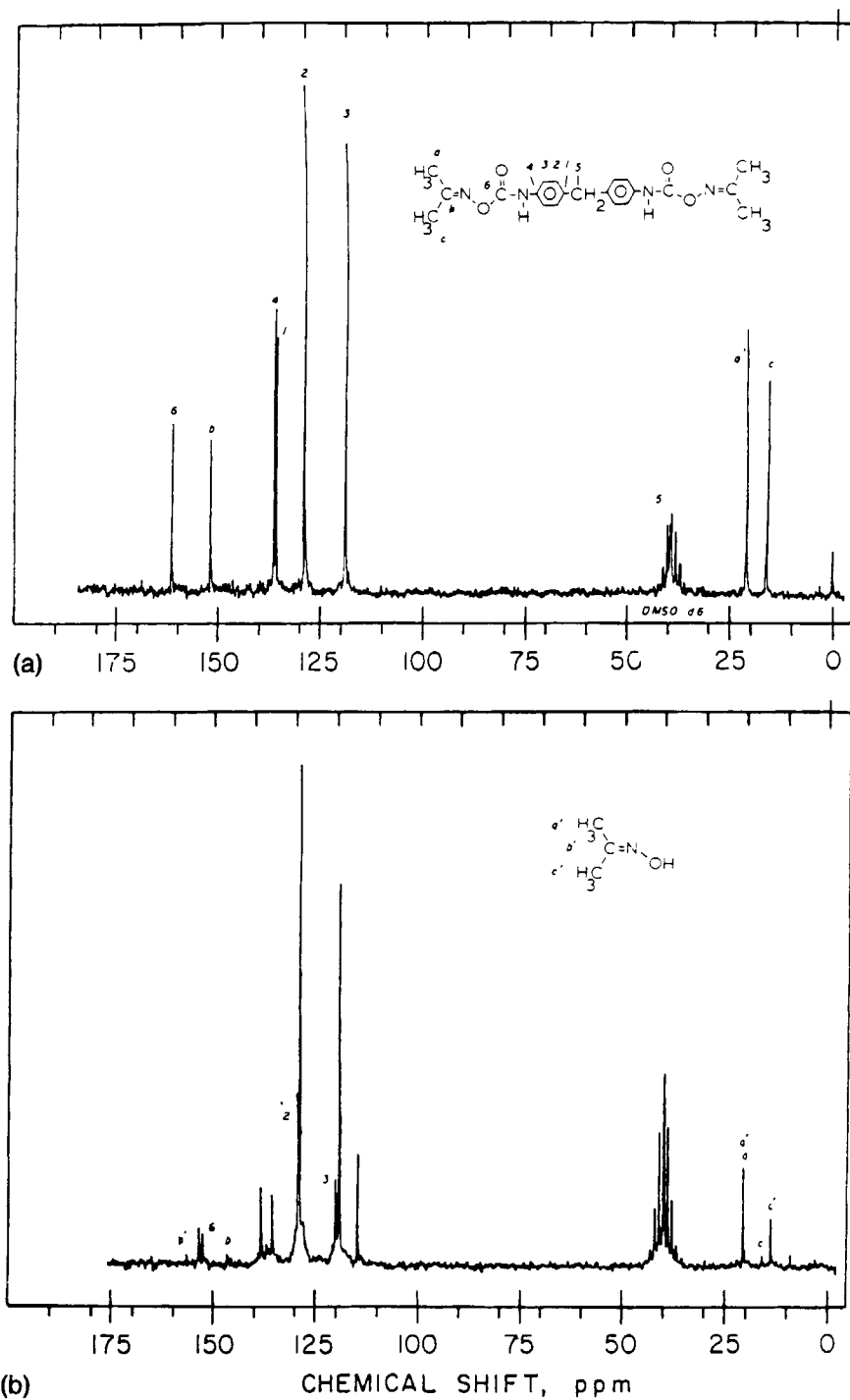


Fig. 2. Carbon-13 NMR spectra of *N,N*-(2-propyloximino)-4,4'-methylenebis(phenyl-carbamate): (a) at 120°C; (b) at 150°C.

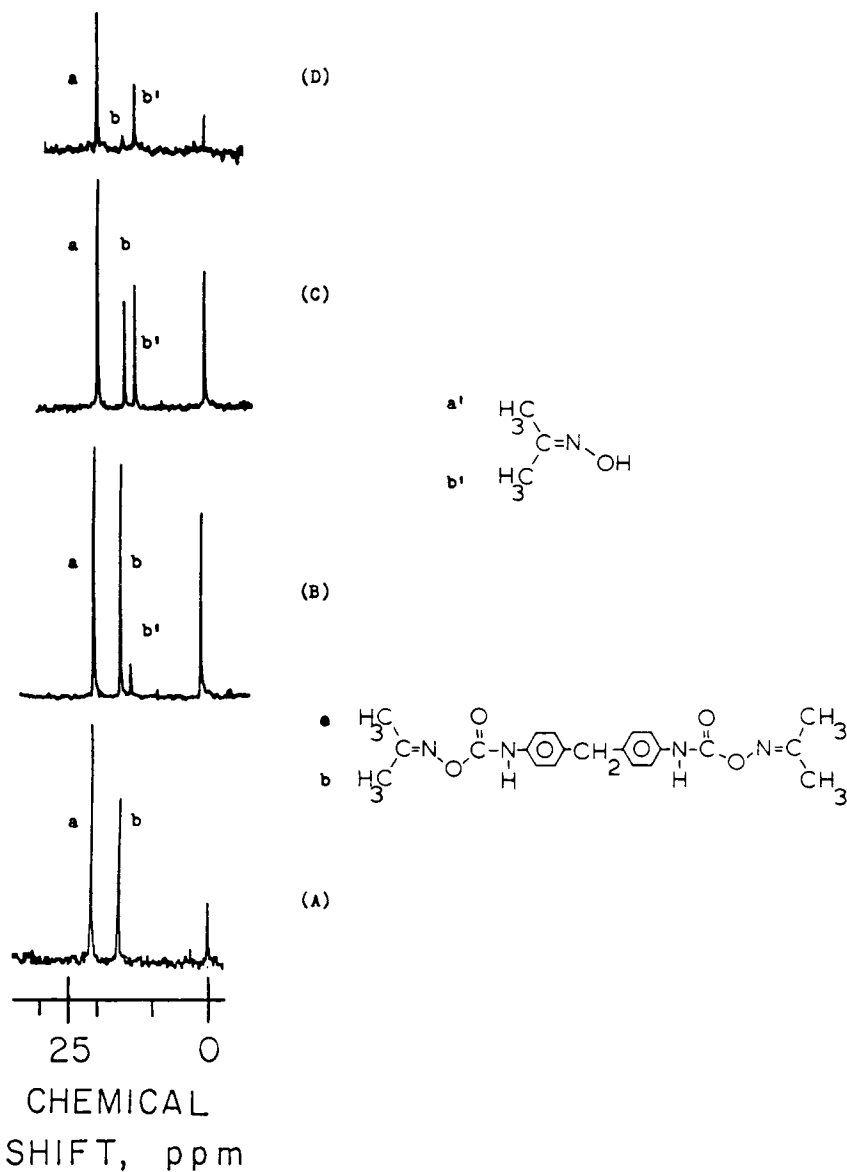


Fig. 3. Carbon-13 NMR spectra of III heated at: (A) 120°C, 24 h; (B) 150°C, 2 min; (C) 150°C, 10 min; (D) 150°C, 60 min.

¹H-NMR. The corresponding proton spectra show the dissociation at 123°C by the appearance of the regenerated acetone oxime. The methyl peaks for the oxime were observed at 1.7 ppm whereas the methyl groups of III appeared at 1.9 ppm. As expected,⁷ the peak due to the OH proton of acetone oxime was too broad to be observed. The NH resonance at 9.5 ppm became less intense upon heating, while a new NH signal appeared at 8.5 ppm, corresponding to a urethane group.

From these data we established that the compound *N,N*-(2-propyloxi-mino)-4,4'-methylenebis(phenylcarbamate) dissociates into the starting ace-

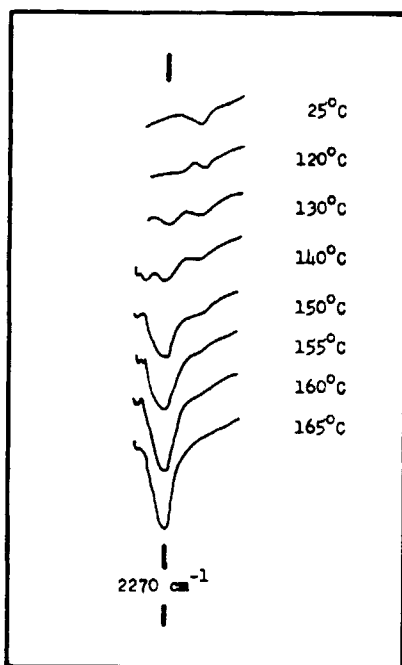


Fig. 4. Infrared spectrum of III on heating at indicated temperatures.

tone oxime and another highly reactive diphenylmethane derivative. NMR data did not verify the regeneration of the isocyanate (MDI); however, a urethane type resonance was observed. We believed that the MDI was regenerated but immediately reacted with trace water known to exist in the DMSO-d₆. The product of that reaction could then react with a second molecule of MDI, etc.

To evaluate the regeneration of MDI, the infrared (IR) spectra of an anhydrous sample of III were taken at temperatures between 20°C and 165°C. Figure 4 shows the —N=C=O peak, at 2270 cm^{-1} , for 120°C and above. Recently solid state NMR has revealed the —N=C=O group in a powdered sample heated to 150°C.⁵ Thus in a dry system, the reaction of III at $> 123^\circ\text{C}$ was shown to "unblock" the acetone oxime from the potential post-polymerization crosslinking agent (PPCA) to yield MDI.

Reactions with Polymers. It has been shown that reacting III with a block copolymer of polyurethane and a polyester can increase the polymer modulus,^{2-4,6} thus suggesting crosslinking. Having shown the structure and unblocking of (III), we thus chose to examine by NMR the reaction of several polymers with this potential PPCA. Three polymer samples, poly(acrylic acid) (PAA), polyacrylamide (PA), and poly(vinyl alcohol) (PVA), were prepared with 2–3% (w/w) of blocked isocyanate (III) and dissolved in DMSO-d₆ (5% w/w). The ¹³C spectra Figures 5(a) and 6(a) were recorded at 120°C. The signals for the methines, methylene, and carbonyl carbons are easily identified for each polymer system. The resonances for III cannot be detected above the noise due to their low concentration (0.1% w/w) in the DMSO-d₆ solution. After heating the three mixtures to 150°C for 10 min, the

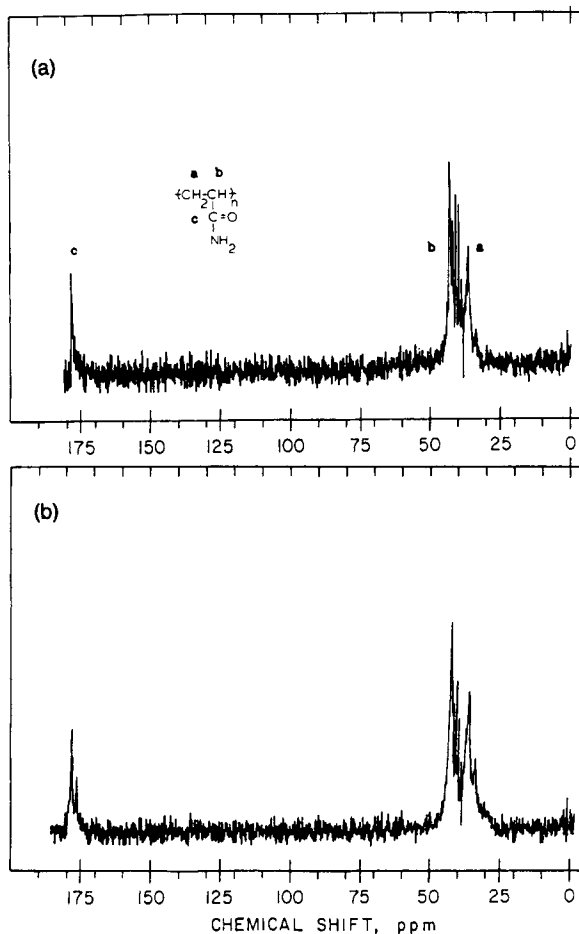


Fig. 5. Carbon-13 NMR spectra of polyacrylamide (a) before and (b) after crosslinking.

solutions were cooled to 120°C and the ^{13}C spectra repeated [Figs. 5(b) and 6(b)].

Both the PAA- and PA-formed viscous gels upon heating while the PVA did not. Crosslinking was confirmed by examination of the carbonyl region (~ 175 ppm) of the spectra. Both the PAA and PA showed a new peak upfield of the original carbonyl, due to the hindered and shielded configuration of the crosslink site. All the peaks in the reacted samples show a slight dipolar broadening, attributable to the lower mobility and solubility of the cross-linked network.⁸

The spectrum of PVA showed no change after heating. We believe that the polymer being hydroscopic may have compromised this experiment. As mentioned earlier water reacts with regenerated MDI to form noncrosslinked products. With this in mind, an excess (10% w/v) of III was added to the original PVA/III sample and the experiments repeated. After heating, the sample remained nonviscous but the ^{13}C showed two new resonances for the CH_2 and CH carbons near the crosslinked site indicating that crosslinking reaction occurred. The reaction of a polymer (PAA) containing labile

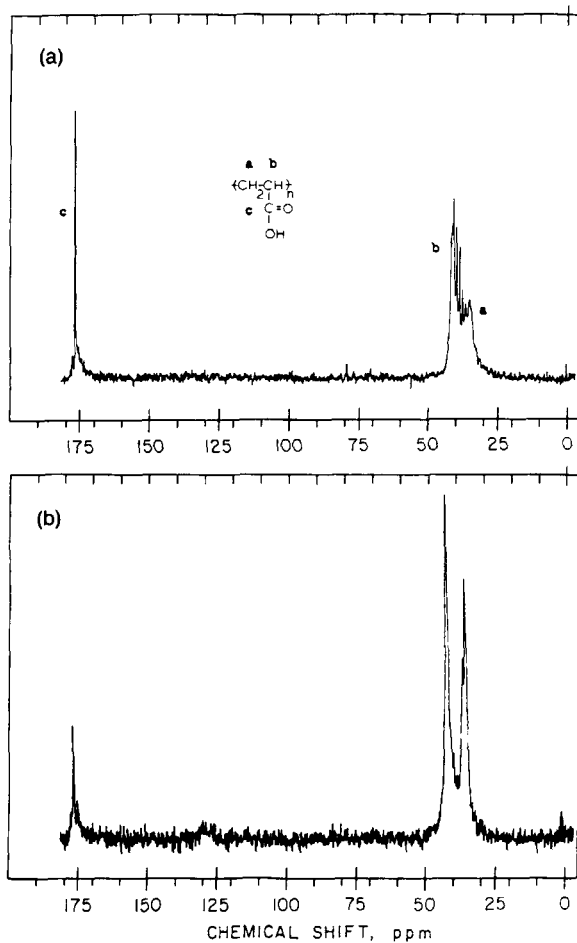
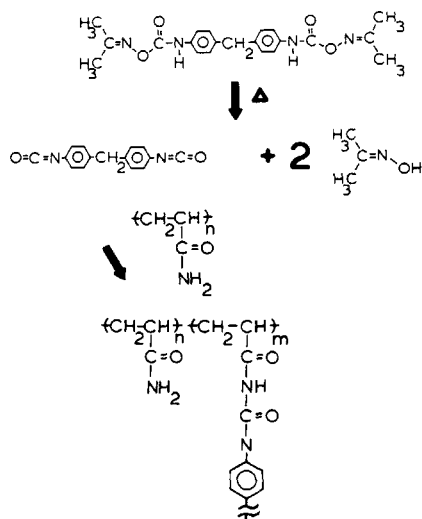


Fig. 6. Carbon-13 NMR spectra of polyacrylic acid (a) before and (b) after crosslinking.

hydrogens with *N,N*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate) is outlined in the following scheme:



CONCLUSIONS

The blocked diisocyanate, *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate), can be used as a "post-polymerization crosslinking agent" (PPCA) with polymers containing labile hydrogen groups. The regeneration of MDI and acetone oxime has been observed, on heating ($> 123^{\circ}\text{C}$), by NMR and IR spectroscopy. The unblocking of MDI upon heating is kinetically controlled reaction.

Crosslinking of three polymer systems, polyacrylic acid, polyacrylamide, and poly(vinyl alcohol) has also been demonstrated, by NMR, to occur when heating a mixture of PPCA and polymer and heating for 150°C for 10 min.

In general *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate) should be useful for many different polymer systems that contain labile hydrogens such as $-\text{NH}$, $-\text{OH}$, and $-\text{SH}$.

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