Polymer 40 (1999) 6597–6605

Polymer Communication

Synthesis of 3-alkylated-1-vinyl-2-pyrrolidones and preliminary kinetic studies of their photopolymerizations

L.A. White[a], S. Jönson[b], C.E. Hoyle[a], L.J. Mathias[a,*]

[a]Department of Polymer Science, University of Southern Mississippi, SS Box 10076, Hattiesburg, MS 39406-0076, USA
[b]Becker Acroma AB, Box 2016, S-195 02, Marsta, Sweden

Received 20 November 1998; accepted 6 March 1999

Abstract

1,6-Bis-3-(vinyl-3-2-pyrrolidonyl)hexane (BNVP) was synthesized for use as a crosslinker in the photopolymerization of 1-vinyl-2-pyrrolidone (NVP). A model compound, 3-hexyl-1-vinyl-2-pyrrolidone (HNVP), was also synthesized for use as a model comonomer in the kinetic studies of NVP copolymerization. Copolymerizations with NVP and low feed ratios of HNVP indicate that alkyl substitution in the 3-position on the pyrrolidone ring does not affect radical reactivity of the monomer. However, the comonomer containing this hexyl side chain acted as an internal plasticizer for the NVP polymers, lowering the T_g and reducing the effect of autoacceleration on the photopolymerization process. The crosslinked polymers exhibited gel-like swelling in water. The crosslinker limited the mobility of the polymer chains early in the polymerization and induced earlier onset of the Tromsdorff effect. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Autoacceleration; Crosslinker; Hydrogels

1. Introduction

N-Vinylpyrrolidone (NVP) is a hydrophilic, nonionic monomer that readily polymerizes thermally or photolytically. NVP is often utilized in UV curable systems owing to the fact that it does not display oxygen inhibition effects so common to free radical polymerizations. Poly(*N*-vinylpyrrolidone) (PNVP) is used in a number of cosmetic applications because of its water solubility and its capacity to function as a compatibilizing surfactant polymer. It has also been investigated for applications in the biomedical field. PNVP has been considered as a plasma substitute, a soluble drug carrier, a modifier for enzymes, and a comonomer in UV curable bioadhesives [1,2]. In both cosmetics and the biomedical field, formation of PNVP hydrogels can be attractive because of the high water uptake of this water-soluble polymer [3].

Hydrogel formation can be difficult due to the low reactivity of NVP with traditional dimethacrylate monomers. The radical reactivity ratios of NVP/methacrylate comonomer systems have vastly different values, leading to only a small amount of NVP being incorporated early in the polymerization [4]. This can lead to difficulty in reproducing hydrogel properties and inconsistent quality of the final products [3]. This work details the synthesis of a novel crosslinker based on NVP itself to eliminate these differences in reactivity ratios between the NVP monomer and the crosslinker. The similarities of the polymerizable moieties, both *N*-vinyl groups, was expected to give random incorporation of the crosslinker with NVP and eliminate inconsistencies in the polymer properties, based on lack of control of the crosslinking process. In addition, the hydrocarbon linker used between the two pyrrolidone rings should be stable to conditions that would be encountered by the hydrogel.

Another interesting aspect of this crosslinker is its potential ability to affect the kinetics of polymerization. Acrylate and methacrylate monomers have been the most well characterized photopolymerization systems to date [5–7]. It has been documented that difunctional acrylate monomers markedly increase the rate of polymerization of monofunctional acrylates under photocure. A similar increase in cure kinetics was expected with this bispyrollidone crosslinker. Such an increase in polymerization rate without compromise of polymer properties is an additional advantage for real-world applications.

---

* Corresponding author. Tel.: +1-601-266-4868; fax: +1-601-266-5504.
E-mail address: lon.mathias@usm.edu (L.J. Mathias)

PII: S0032-3861(99)00189-5

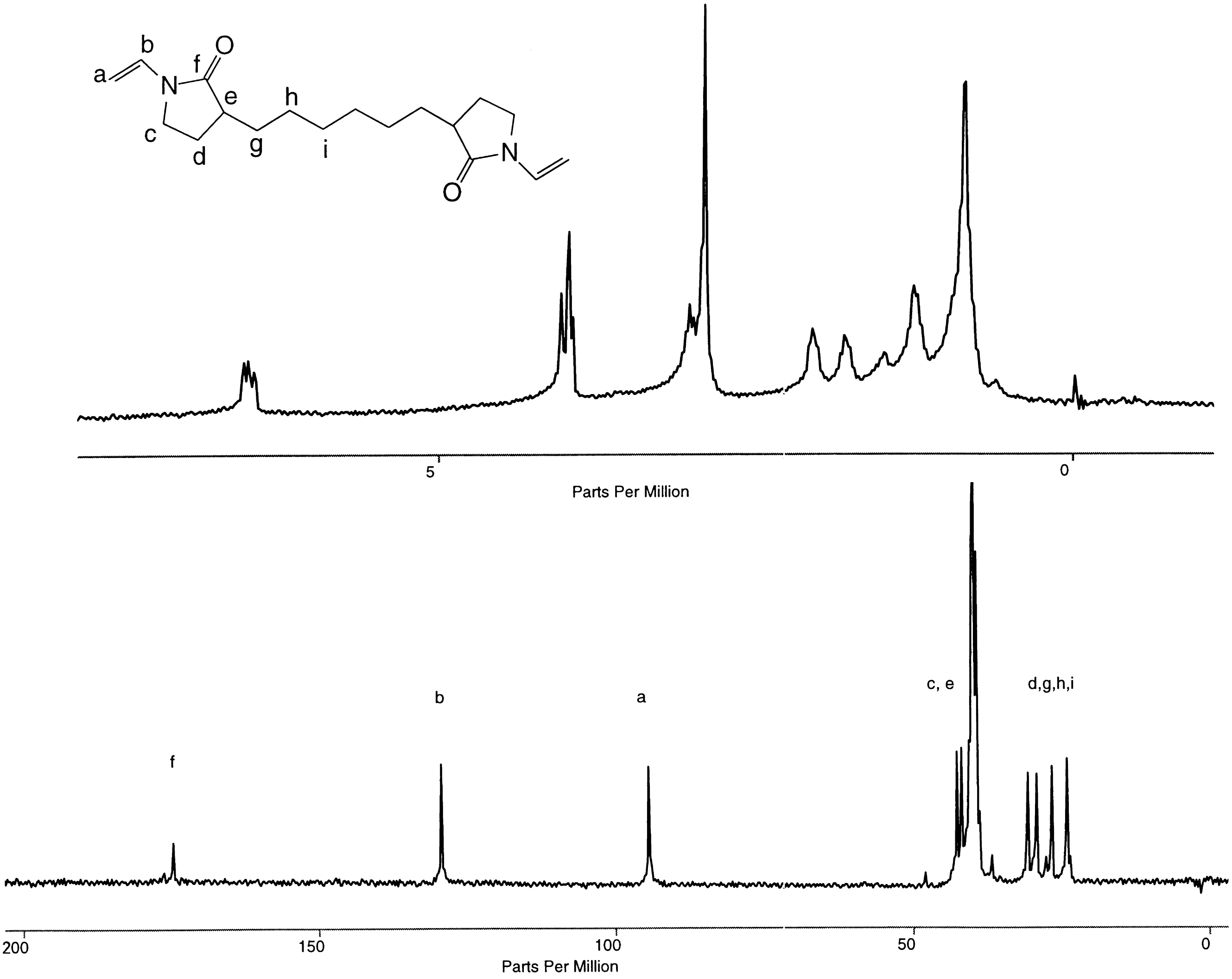


Fig. 1. ^1H and ^{13}C NMR of BNVP.

2. Experimental section

2.1. Materials

All the reagents were purchased from Aldrich Chemical Company unless otherwise noted. NVP was distilled under vacuum to remove the inhibitor. Tetrahydrofuran (THF) was dried over calcium hydride and distilled prior to use.

2.2. General procedures

IR spectra were obtained on an ATI-Mattson Galaxy 5020 spectrometer. Solution ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer at 300.133 and 75.47 MHz respectively with standard acquisition parameters. Letters in spectral data in the experimental section refer to ^{13}C NMR peak assignments in Figs. 1 and 2. Photopolymerization kinetic studies were carried out using a DuPont 830 Differential Photocalorimeter (DPC). Thermogravimetric analyses (TGA) were performed on a TA Instruments Simultaneous TGA-DTA 2960 module (2100 data station) at a heating rate of 20°C/min in an N_2 atmosphere. Differential scanning calorimetry (DSC) was conducted on a TA Instruments 2920 DSC module (2100 data station) at a heating rate of 10°C/min in an N_2 atmosphere.

2.3. Synthesis of 3-Hexyl-1-Vinyl-2-Pyrrolidone

All the glassware was dried overnight in a drying oven prior to use. A 100 ml three-neck flask was fitted with an addition funnel, N_2 inlet, and rubber septa. The flask was charged with lithium diisopropylamide (LDA) (46 ml, 2.0 M solution in hexane/THF/ethylbenzene, 0.092 mol) and THF (9 ml), and stirred in a −78°C bath. NVP (10 ml, 0.091 mol) and THF (10 ml) were added dropwise over 30 min. The reaction was stirred for an additional 30 min. 1-Bromohexane (11.9 ml, 0.085 mol) was added dropwise to the reaction vessel and stirring continued at −78°C for 30 min then at room temperature for 2 h. The reaction color changed from dark red to yellow over the

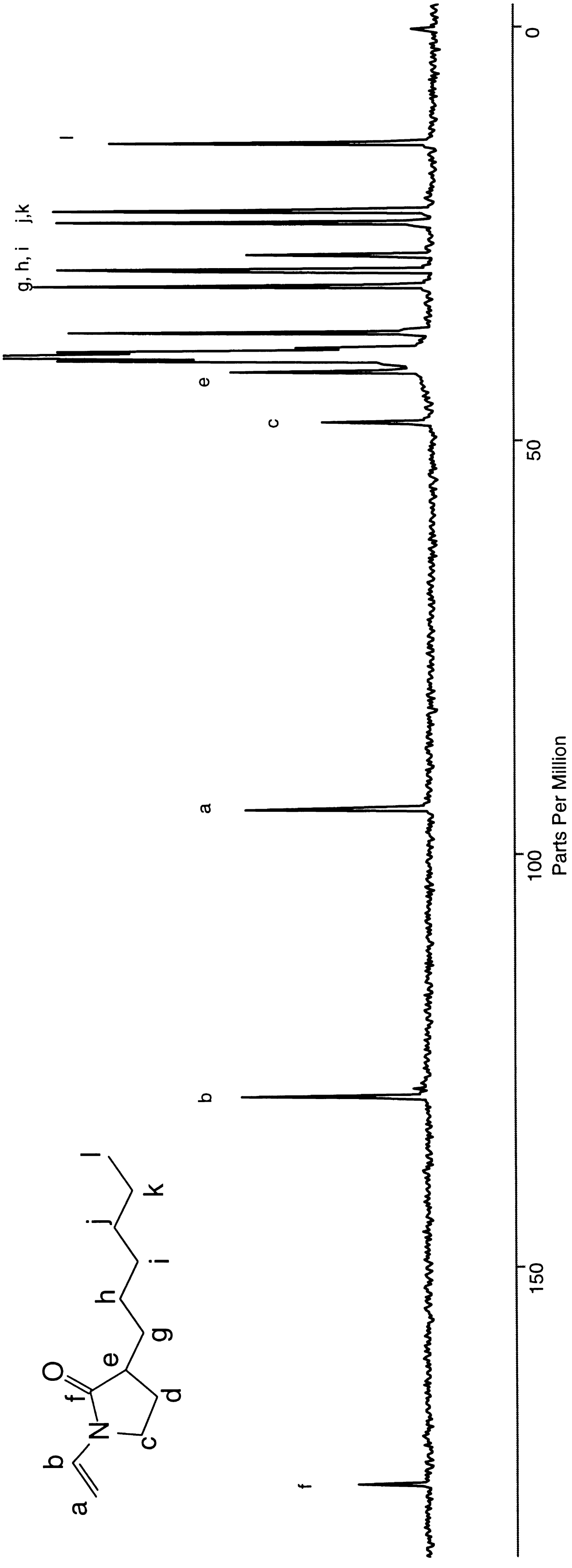
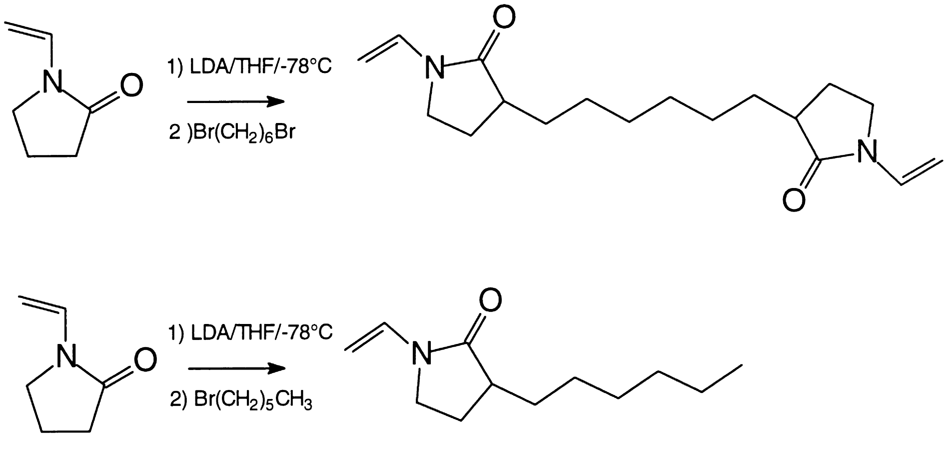


Fig. 2. ^{13}C NMR of HNVP.



Scheme 1.

course of the reaction. The reaction was quenched with 50 ml deionized (DI) H_2O, and the organic layer was separated. The aqueous layer was extracted three times with equal volumes of diethyl ether. The organic layers were combined and concentrated (Büchi rotary evaporator). The product was purified by column chromatography with silica gel using hexane as a separation solvent to give a yellow liquid (overall yield: 37%); IR (NaCl plate, cm^{-1}) 2965, 2934, 2862, 1708, 1625, 1491, 1460, 1429, 1378, 1327, 1275, 1254, 1038, 986, 842, 708, 584; ^1H NMR (DMSO-d_6, δ) 1.64 (s, 3H, $-CH_3$), 1.84 (t, 2H, $-CH_2-$), 2.20 (t, 4H, $2-CH_2-$), 2.72 (t, $-CH_2-$), 4.13 (s, 1H, –CH–), 5.22 (t, 2H, vinyl methylene), 7.74 (m, 1H, vinyl methine); ^{13}C NMR (DMSO-d_6, δ) 14.13 (1), 22.25 (k), 23.75 (j), 27.52 (i), 29.41 (h), 31.34 (g), 41.75 (c), 47.90 (e), 94.66 (a), 129.39 (b), 176.37 (f).

2.4. Synthesis of 1,6-(Bis-3-vinyl-2-pyrroldionyl)hexane

All the glassware was dried overnight in a drying oven prior to use. A 100 ml three-neck flask was fitted with an addition funnel, N_2 inlet, and rubber septa. The flask was charged with LDA (41 ml, 2.0 M solution in hexane/THF/ethylbenzene, 0.082 mol) and THF (9 ml) and stirred in a −78°C bath. NVP (9 ml, 0.082 mol) in THF (9 ml) was added dropwise over a span of 30 min. The reaction was stirred for an additional 30 min. 1,6-Dibromohexane (13 ml, 0.08 mol) was added dropwise to the reaction vessel. The reaction was stirred at −78°C for 30 min then stirred at room temperature for 2 h. The reaction color changed from dark red to yellow-orange over the course of the reaction. The reaction was quenched with 50 ml DI H_2O. The organic layer was separated, and the aqueous layer was extracted three times with equal volumes of diethyl ether. The organic layers were combined and concentrated (Büchi rotary evaporator). The product was purified by silica gel column chromatography (30% hexane/70% ethyl acetate, v/v) to give a yellow waxy solid (mp 27°C) (overall yield: 17%); IR (NaCl plate, cm^{-1}) 2933, 2856, 1696, 1631, 1487, 1458, 1420, 1386, 1329, 1256, 1036, 978, 844, 724, 695, 604; ^1H NMR (DMSO-d_6, δ) 1.24 (t, 3H, $-CH_3$), 1.48 (t, 2H, $-CH_2-$), 1.79 (t, 2H, $-CH_2-$), 2.01 (t, 2H, $-CH_2-$), 2.97 (t, 2H, $-CH_2-$), 4.02 (m, 4H, ring $-CH_2-$), 6.50 (m, 3H, vinyl $-CH_2-$ and –CH); ^{13}C NMR (DMSO-d_6, δ) 23.84 (i), 26.43 (h), 28.83 (g), 30.64 (d), 41.43 (e), 42.63 (c), 94.12 (a), 129.18 (b), 174.58 (f).

2.5. Synthesis of 1-hexyl-2-pyrrolidone

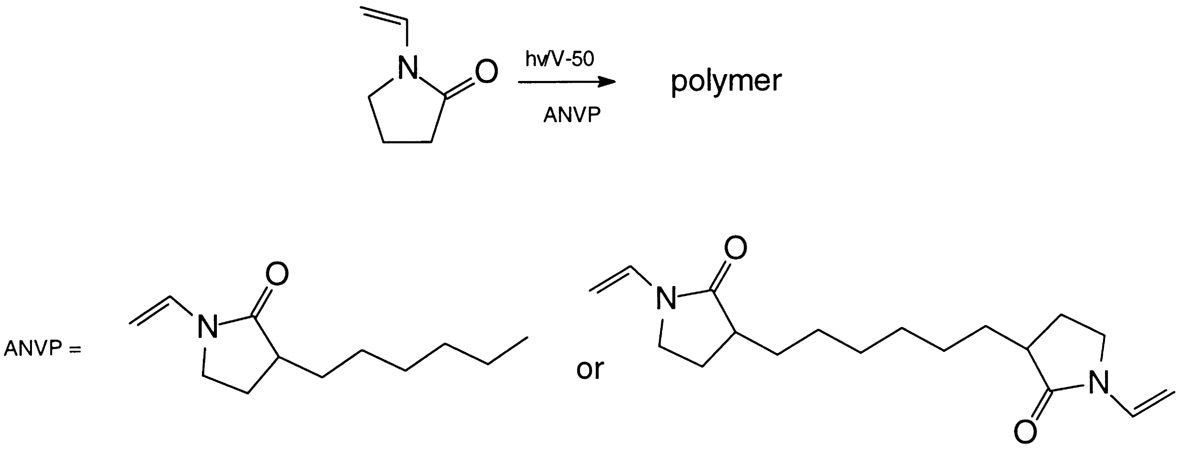
A 100 ml 3-neck round bottom flask fitted with a nitrogen inlet and a reflux condenser was charged with 2-pyrrolidone (1.5 ml; 21 mmol), 1-bromohexane (2.8 ml, 20 mmol), K_2CO_3 (6.9 g, 2.1 eq.), and DMF (20 ml). The reaction mixture was stirred at 100°C for 6 h. The yellow liquid was filtered to remove the solid K_2CO_3 and washed with 5% HCl. The product was extracted with hexanes and concentrated by rotary evaporation (overall yield: 65%); IR (NaCl; cm^{-1}): 2958, 2931, 2859, 1747, 1710, 1467, 1401, 1255, 1191, 1069, 1057, 1031, 912, 792. ^1H NMR ($CDCl_3$; δ): 0.80 (t, 3H, $-CH_3$), 1.22 (m, 2H, $-CH_2-$), 1.4 (t, 2H, $-CH_2-$), 1.57, (t, 2H, $-CH_2-$), 3.33 (2H, $-CH_2-$), 4.02 (m, ring $-CH_2-$), 6.23 (m, 2H, $-CH_2$); ^{13}C NMR ($CDCl_3$; δ): 13.93 ($-CH_3$), 22.53 ($-CH_2-$), 25.47 ($-CH_2-$), 27.89 ($-CH_2-$), 28.52 ($-CH_2-$), 28.70 ($-CH_2-$), 31.43 ($-CH_2-$), 31.74 ($-CH_2-$), 32.84 ($-CH_2-$), 155.46 (CO).

2.6. Homopolymerization of HNVP

HNVP was homopolymerized in bulk using a mercury lamp and Irgacure-651 (Ciba-Geigy; 0.5 mol%) in the DPC. The polymer sample was extracted with acetone and dried overnight under reduced pressure. Overall polymerization conditions are depicted in Scheme 2.

2.7. Copolymerization of NVP and HNVP

Monomer solutions (20 M in DI H_2O) consisting of NVP and HNVP were prepared with various comonomer molar ratios (2, 5, 10 and 15%). To the solutions was added V-50



Scheme 2.

(Wako Chemical) aqueous initiator (0.5 mol%) with stirring. Aliquots were photopolymerized after a 30 min nitrogen purge in a DPC using a mercury lamp for kinetic studies. Polymers were dissolved in DI H_2O and reprecipitated into acetone. Polymers were dried overnight under reduced pressure at 65°C.

2.8. Crosslinking of NVP with BNVP

Monomer solutions (20 M in DI H_2O) were prepared using various molar ratios of BNVP as a crosslinker (0.25, 0.5, 1 and 2%). Solutions were initiated and photopolymerized as copolymers as described earlier. Large-scale polymerizations were carried out in sealed test tubes under nitrogen purge. Monomer solutions were purged with nitrogen gas for 30 min prior to polymerization. Polymers were swelled and extracted with DI H_2O and dried overnight under reduced pressure at 65°C.

3. Results and discussion

3.1. Monomer and crosslinker syntheses

The same general procedure was used for both the HNVP monomer and the BNVP crosslinker. The conditions for substitution in the alpha position to the carbonyl were used in accord with a previously published procedure used to synthesize 3-allyl-1-vinyl pyrrolidone [8]. An inverse addition procedure was used (Scheme 1) in which NVP was added dropwise to LDA to form the resonance stabilized anion before addition of the brominated species. A side

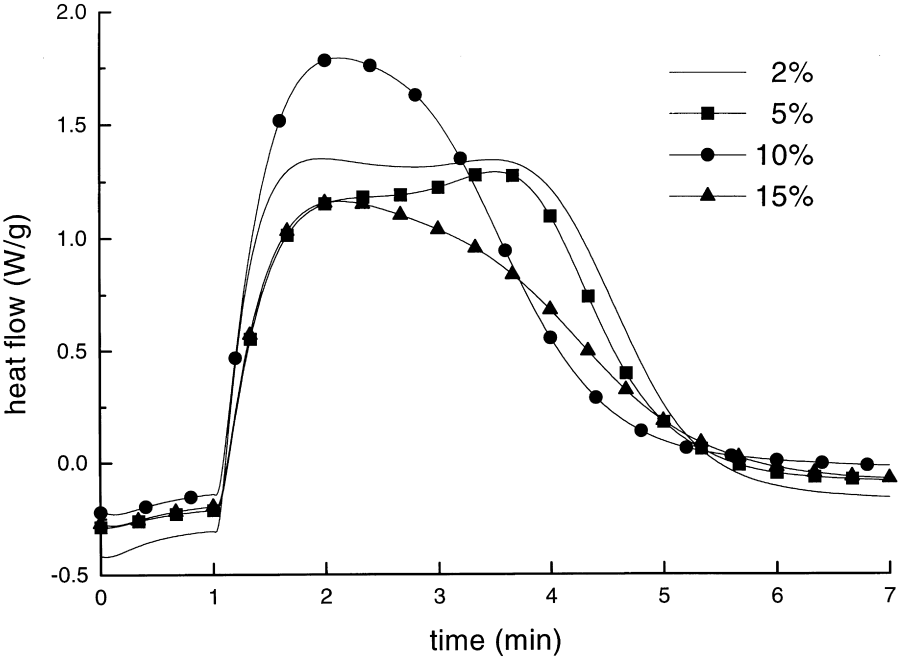


Fig. 3. DPC thermograms of NVP with varying feed ratios of HNVP comonomers.

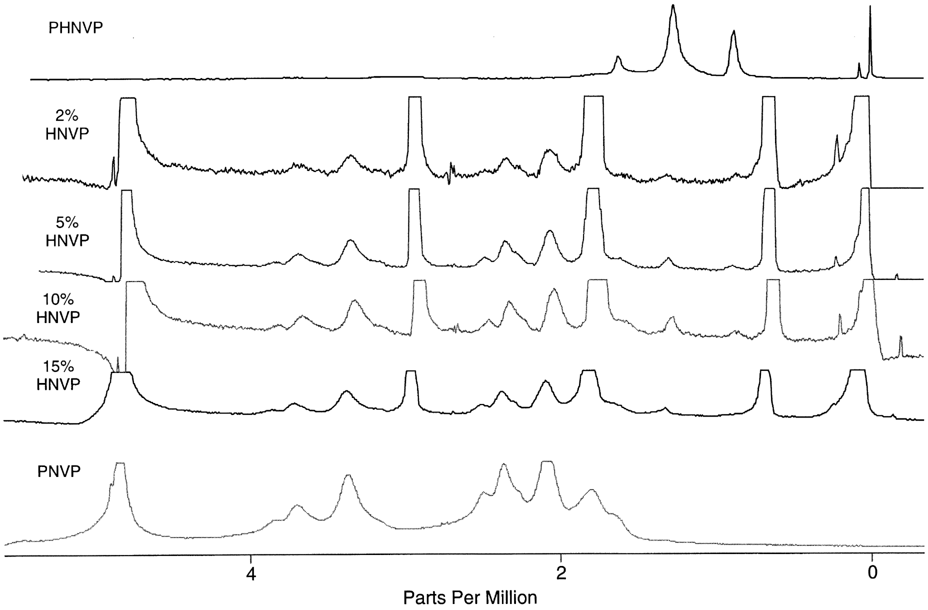


Fig. 4. ^{1}H NMR spectra of VHP and PVP with varying ratios of HNVP comonomer.

product was observed by gas chromatography (GC) but was not isolated. The side product and the residual starting material (brominated species) were removed from the reaction mixture via silica gel chromatography. Structures were confirmed using FT-IR (Fig. 5, Fig. 7) as well as ^{1}H (Fig. 4) and ^{13}C NMR (Figs. 1 and 2).

3.2. Copolymerization of NVP and HNVP

Incorporation of the crosslinker into the polymer chain was expected to proceed at nearly identical rates owing to the similar nature of polymerizable moiety of the monomer and the crosslinker. To verify this supposition, HNVP was copolymerized with NVP in order to estimate reactivity ratios. The solubility of the less polar HNVP was limited in the aqueous polymerization media, but NVP comonomer aided in solubility. As BNVP as a crosslinker is only expected to be used in low quantities for most applications, feed ratios of less than 15 mol% were sufficient for the purpose of this study.

FTIR spectroscopy of this series of copolymers (Fig. 5) illustrates the incorporation of the HNVP comonomer into

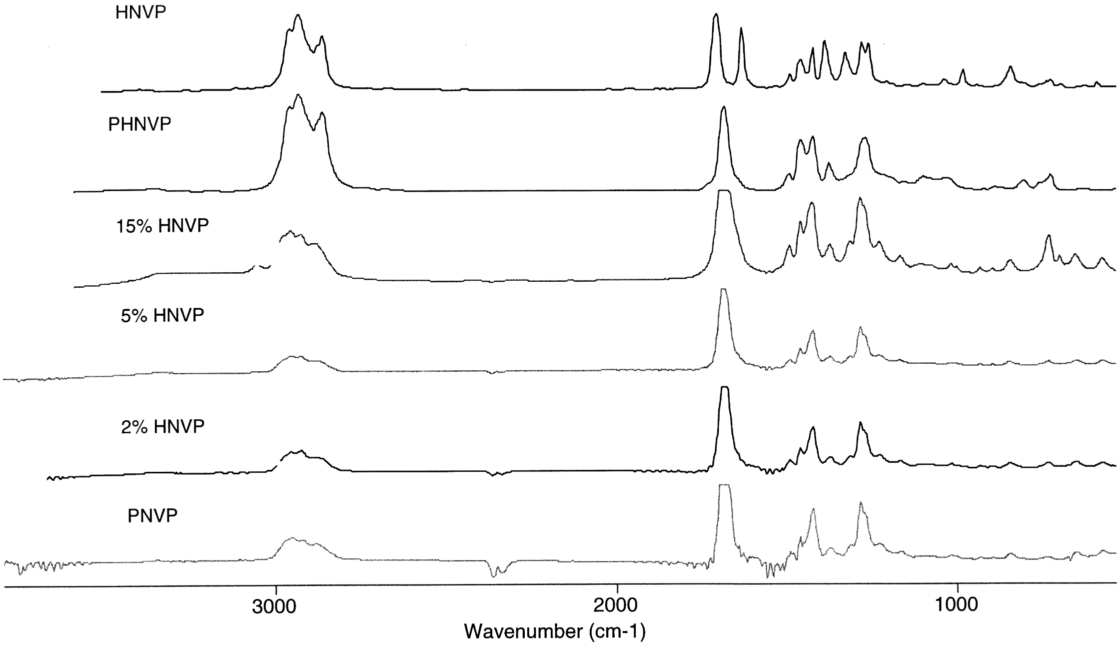


Fig. 5. IR spectra of VHP monomer, homopolymer, and NVP/HNVP copolymers.

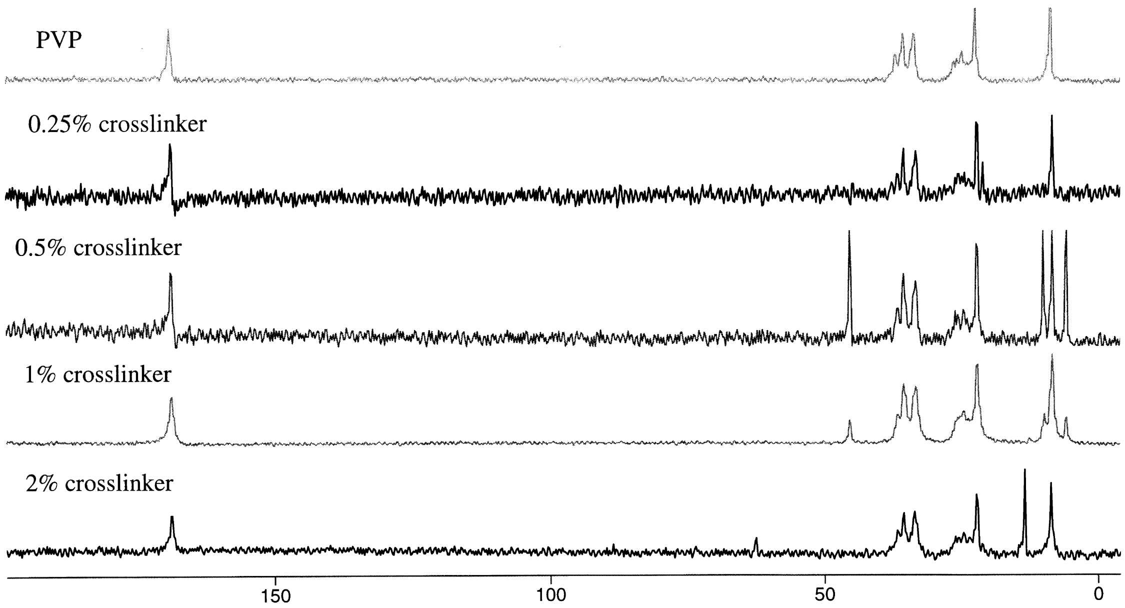


Fig. 6. ^{13}C NMR spectra of PNVP with varying amounts of BNVP crosslinker.

the polymer backbone. The appearance of peaks characteristic for HNVP appear in both the 2 and 5% copolymer in the fingerprint region and are more strongly seen in the 10% and 15% copolymer. These results indicate that the comonomer is incorporating into the predominantly NVP polymer backbone. The disappearance of the peak at 1640 cm^{-1} due to vinyl bonds indicates that the polymers are free of residual monomer.

The kinetics of these photocopolymerizations yielded surprising results (Fig. 3). It was expected that the kinetics of the copolymerizations with varying percentages of the HNVP comonomer would be very similar to the kinetics of NVP homopolymerization under identical conditions. The lowest incorporation of comonomer, 2%, showed practically identical rates to NVP homopolymerization, with an initial exotherm upon the application of UV light followed by a slight increase in the rate at around 3.5 min of exposure due to the onset of the Tromsdorff effect as increasing amounts of high molecular weight polymer caused viscosity-induced increases in the overall rate of polymerization. The 5% copolymer showed the same initial increase in rate although the rate increase due to Tromsdorff was less significant. The 10% copolymer did not show autoacceleration although the initial rate of polymerization was higher for this copolymer than for the polymers with lower comonomer incorporation. The alkyl side chain of the comonomer serves as an internal plasticizer for the polymer, lowering the glass transition temperature and viscosity of the polymerization mixture. Increased chain mobility throughout the polymerization apparently eliminates the Tromsdorff effect. The 15% copolymer showed a slower rate than that of copolymers with lower incorporation of comonomer. The limited water solubility of the HNVP monomer at this percentage in the feed is believed to cause formation of micelles, which change the kinetics of polymerization. The final percent conversion of all copolymers (with the exception of the 15% HNVP feed composition) were similar. The 15% HNVP copolymer also had a lower overall conversion than the other copolymers under similar conditions.

The model compound, *N*-hexyl pyrollidone (NHP), was synthesized to further investigate the kinetic behavior of this system. Polymerizations of NVP in the presence of NHP as an additive were carried out in the same ratios and under identical conditions as those using HNVP as the comonomer. This allowed the investigation of the effect of the hexyl chain as an external plasticizer attached to a non-polymerizable moiety. Surprisingly, the overall rates of the polymerization of NVP did not change with the addition of NHP. The initial rates and the onset of Tromsdorff remained similar to those of NVP without either additive or comonomer. Again, the solubility of the additive in aqueous media is limited due to the hexyl chain, and it is conceivable that hydrophobic effects prevented the additive from behaving as an actual plasticizer during polymerization.

3.3. Crosslinking of NVP with BNVP

Crosslinked NVP was synthesized using BNVP. The amount of crosslinker used in these polymers was kept below 2 mol% as potential applications of these systems would require only small amounts of crosslinker to give desirable properties. In addition, this low feed ratio of BNVP should eliminate any problem with limited solubility in aqueous media as observed in the NVP–HNVP model copolymer systems, although the second pyrollidone ring of the crosslinker may allow greater solubility. The most lightly crosslinked polymers (0.25 mol% BNVP) were soluble in water. At 0.5% and above, the polymers were

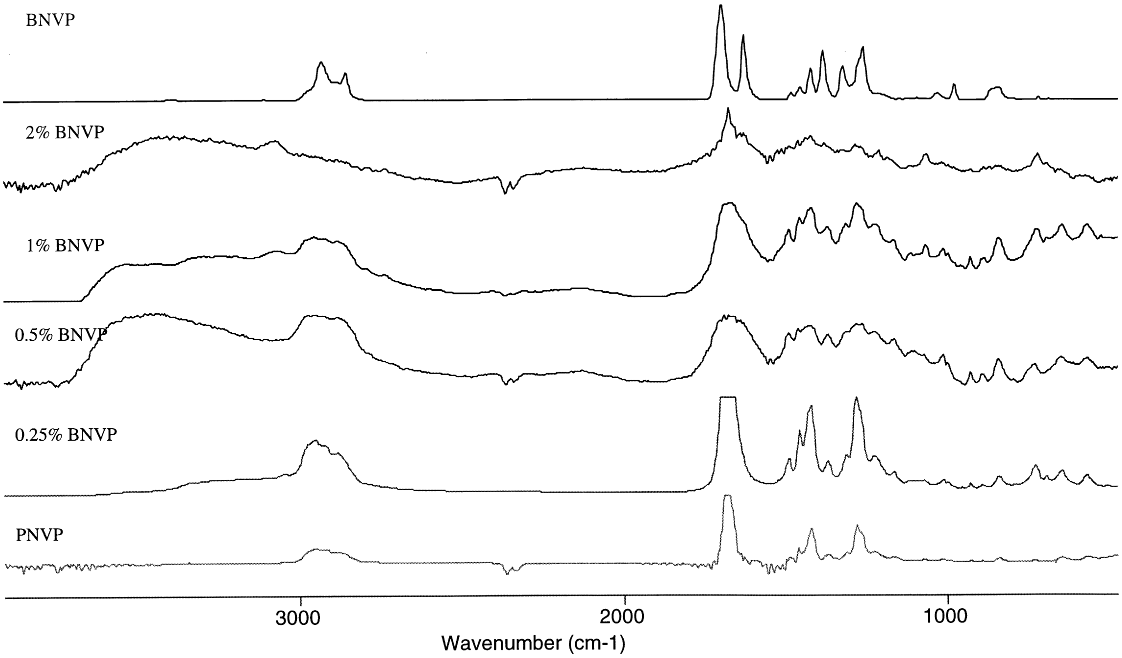


Fig. 7. IR spectra of BNVP and crosslinked PNVP with varying feed ratios of BNVP.

insoluble but exhibited gel-like swelling in water. All of the polymers showed high water uptake and solution NMR spectroscopy was used to verify the polymer structure (Fig. 6). FT-IR spectroscopy was also used to verify the structures (Fig. 7). As in the NVP–HNVP model copolymer system, a series of peaks in the fingerprint region further indicated that incorporation of the crosslinker had taken place.

PNVP is a very hydrophilic polymer [3]. All polymer samples made here were dried at elevated temperature under reduced pressure before thermogravimetric analyses was performed (Fig. 9). Even so, pure PNVP showed a 20% weight loss ending at near 200°C. The weight losses seen in the TGA thermograms of the crosslinked samples between 170 and 300°C are attributed to loss of tightly bound water and breakdown of the crosslinker itself or loss of the hexyl chains that are attached to the carbon alpha to the carbonyl. The percentage of weight lost during these transitions increases with the increasing percentage of the crosslinker. These small weight losses occurred prior to the onset of polymer backbone degradation. A similar phenomenon was seen in the NVP–HNVP model copolymer system.

The kinetics of polymerization with the bispyrollidone crosslinker are shown in Fig. 8. At lower incorporations of

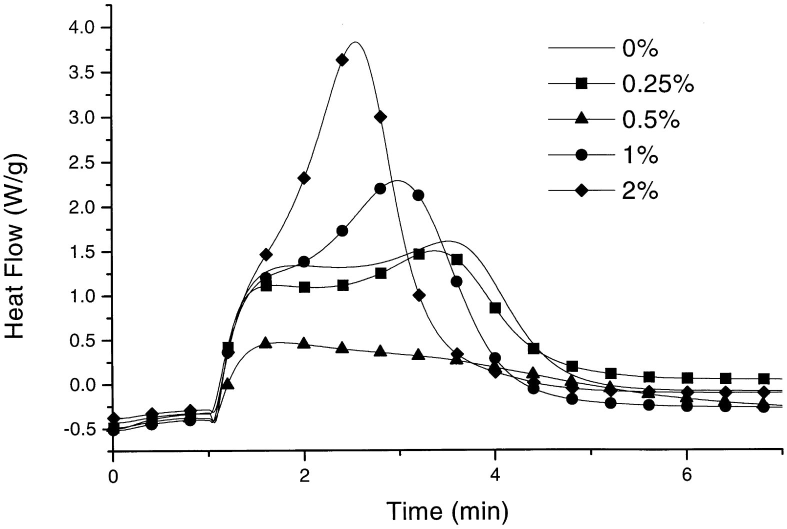


Fig. 8. DPC thermograms of NVP crosslinked with BNVP.

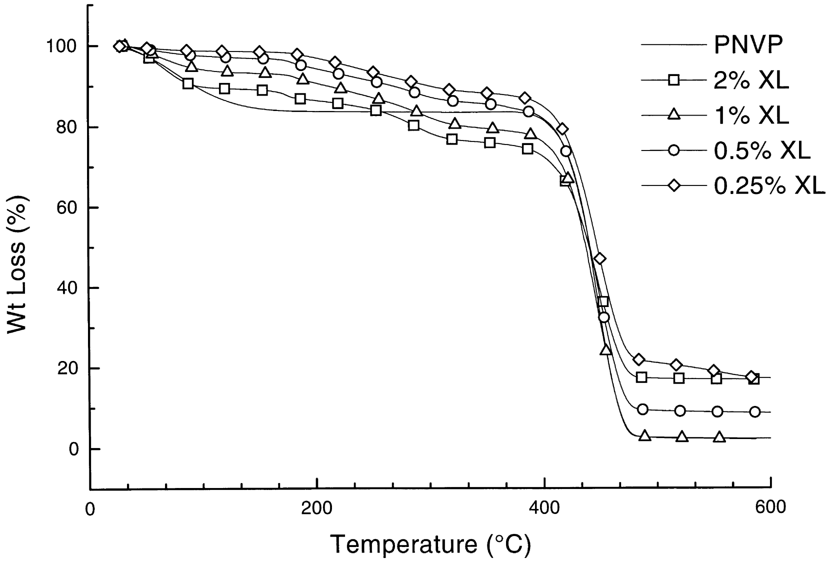


Fig. 9. TGA thermograms of NVP with varying amounts of BNVP crosslinker.

crosslinker, polymerization kinetics were identical to or slower than NVP under similar conditions. At higher feed ratios of crosslinker, the onset and the intensity of the Tromsdorff effect occurred progressively earlier in the polymerizations. At 2% BNVP, the onset occurred almost immediately, indicating very rapid reaction.

4. Conclusions

A novel crosslinker has been synthesized for use in UV curing of NVP. The crosslinker was based on NVP to allow random incorporation into the growing polymer chain and to allow the kinetics of NVP polymerization to be preserved or enhanced by addition of this crosslinker. The crosslinker increased the rate of polymerization of NVP by inducing earlier onset of the Tromsdorff effect. It did not decrease the conversion of monomer to polymer. The thermal characteristics of these crosslinked systems showed that the hexyl linker in the crosslinker had lower stability than the polymer backbone due to the attachment of alpha to the carbonyl. The crosslinked polymers were readily swellable in water. The gels formed using BNVP could easily be tailored by adjusting the crosslink density of the polymers.

Acknowledgements

This work was supported in part by a grant from Becker Acroma, Marsta, Sweden.

References

[1] Ranucci H, Spagnoli G, Sartore L, Bignottie F, Ferruti P. Macromol Chem Phys 1995;196:763.
[2] Kao F, Manivannan G, Sawan S. J Biomed Mater Res 1997;38:191.
[3] Lai Y. J Poly Sci Part A 1997;6:1039.
[4] Young LJ. In: Brandrup J, Immergut EH, editors. Polymer handbook, 3. New York: Wiley, 1974.
[5] Kloosterboer JG. Adv Polym Sci 1988;84:1.
[6] Roofey CG. Photopolymerization of surface coatings. New York: Wiley, 1981.
[7] Reiser A. Photoreactive polymers. New York: Wiley, 1981.
[8] Chockalingam K, Harichian B, Bauld NL. Syn Commun 1990;20:189.