

Copolymerization of N-Vinyl Pyrrolidinone with Multifunctional Acrylates

*Timothy J. White
William B. Liechty
C. Allan Guymon*

*University of Iowa
Department of Chemical and Biochemical Engineering
Iowa City, IA 52246*

Abstract

Despite the common use of N-vinyl pyrrolidinone (NVP) in industrial formulations, the reactivity of NVP and acrylate has not been well studied, particularly in highly functional systems. This work examines the photopolymerization kinetics, mechanical and thermal properties of polymer networks formed from the copolymerization of NVP and acrylate monomers with 1-5 acrylate groups. Interestingly, though NVP increases the rate of polymerization in all acrylate monomers studied, the relative rate increase with NVP content increases with monomer functionality. Such behavior is directly related to the copolymerization characteristics of NVP and acrylate including the prevalence of reaction diffusion termination. Examination of acrylate/NVP systems is compared to copolymerization of acrylate monomer with N-vinyl caprolactam and hexyl acrylate.

Introduction

Overcoming oxygen inhibition of free radical polymerization is a costly endeavor for the photopolymerization industry. Significant research, both industrial and academic, has focused on cost-effective solutions that either remove oxygen from the reacting environment¹ or add molecules that reduce the impact of molecular oxygen²⁻⁴. As early as 1977, N-vinyl pyrrolidinone (NVP) was reported to significantly decrease oxygen inhibition in acrylate systems.⁵

NVP is a common additive to photopolymer systems acting as a reactive diluent that increases polymerization rate and conversion in the presence of oxygen. Despite the frequent inclusion of NVP in acrylate systems, the copolymerization kinetics are not well understood especially in multifunctional acrylate systems. As a common component in contact lenses, the basic copolymerization behavior of NVP and methacrylates has been reported.⁶⁻⁸ In addition, Miller and Hoyle examined the copolymerization of NVP and other N-vinyl amides with the common diacrylate 1,6-hexanediol diacrylate (HDDA) in air.^{9,10}

Our previous examination of the influence of NVP in the formation of holographic polymer dispersed liquid crystals (HPDLCs) has shown that NVP is influential on liquid crystal phase separation as NVP serves to solubilize the mixture to higher double bond conversions.¹¹ The reactive synergy between NVP and the pentaacrylate (DPPA) in HPDLCs was examined in detail. Increasing NVP concentration increased polymerization rate and acrylate conversion substantially. Interestingly, after complete conversion of NVP, further acrylate monomer conversion was not observed. This coupling of the conversion of NVP and acrylate in this highly crosslinked polymer was attributed to reaction diffusion termination.

Similar behavior is expected in simple copolymerization of NVP and acrylate. To this end, we have examined the polymerization kinetics of the copolymerization of NVP and acrylate monomers with one to five acrylate double bonds with photo-differential scanning calorimetry (PDSC) and real-time IR (RTIR). These polymerization kinetic results are compared to mechanical and thermal properties of NVP/acrylate copolymers by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The similar molecule N-vinyl caprolactam was also studied under similar conditions. The influence of reaction diffusion termination on the copolymerization is discussed.

Materials and Methods

Materials

All copolymerizations of NVP and acrylate were initiated by 0.2 wt% of Darocur 4265 (DC-4265, Ciba), a 50 wt% mixture of 2-hydroxy-2-methyl-1-phenyl-propanone (Darocur 1173) and diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (Darocur TPO). Multifunctional monomers chosen for this study were based on similar structures: diethylene glycol diacrylate (DEGDA, Sartomer), trimethylpropane triacrylate (TMPTriA, Sartomer), di-trimethylpropane tetraacrylate (DTMPTetA, Sartomer) and dipentaerythritol pentaacrylate (DPPA, Sartomer). The copolymerization of N-vinyl pyrrolidinone (NVP, Aldrich) and N-vinyl caprolactam (NVC, Aldrich) was also compared to the monofunctional hexyl acrylate (HA, Aldrich). All chemicals were used as received. The chemical structures of the monomer used in this study are shown in Figure 1.

Methods

The polymerization kinetics were studied by the complementary techniques of photo-differential scanning calorimetry (PDSC) and real-time IR (RTIR). PDSC has been frequently used in the examination of photopolymerization as a direct determination of polymerization rate. The PDSC used is a Perkin Elmer Diamond DSC with a medium pressure Hg-Xe arc lamp (Ace Glass). The light source was filtered to 365 nm with a bandpass filter (Omega Optical). Light intensity for all PDSC study was $2.5 \pm 0.2 \text{ mW/cm}^2$. Unless otherwise noted, samples were purged with nitrogen for five minutes before polymerization.

RTIR, a direct examination of double bond conversion, is a useful tool in understanding copolymerization. RTIR enables direct conversion analysis of two distinct functional groups. The RTIR is a Thermo Electron Nexus 670 FTIR, adapted with a horizontal transmission accessory.¹² The FTIR bench and horizontal transmission accessory are purged with nitrogen to remove the presence of carbon dioxide and water vapor. Photopolymerization was initiated with an EFOS Acticure 4000 UV lamp, filtered to 365 nm. Light intensity for all RTIR experiments was 2.5 mW/cm^2 . Double bond conversion was analyzed at the acrylate peak at 810 cm^{-1} and the NVP peak at 1334 cm^{-1} .

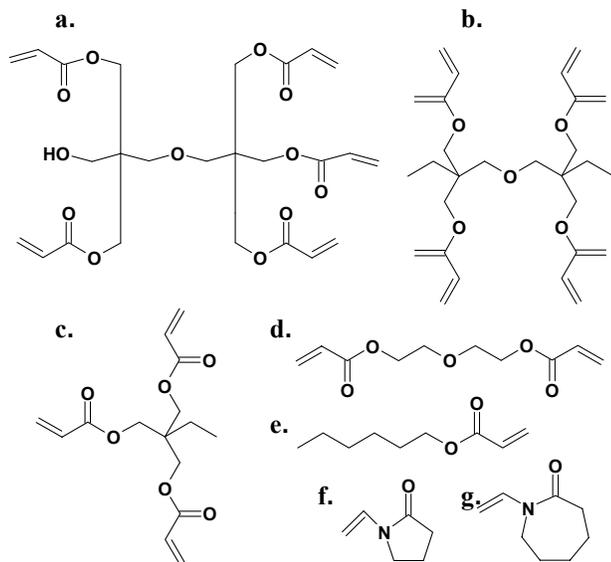


Figure 1. Chemical structures for the monomers used in this study. (a) DPPA, (b) DTMPTetA, (c) TMPTriA, (d), DEGDA, (e) HA, (f) NVP and (g) NVC.

The influence of NVP on polymerization kinetics was correlated to mechanical properties through dynamic mechanical analysis (DMA). The DMA used here is a TA Instruments Q800. Polymer bars of dimension 1 cm by 4 cm by 2 mm were polymerized for 10 minutes at 1.5 mW/cm² with a Black-Ray monochromatic (365 nm) lamp in a purged tank. To determine Young's modulus, samples were clamped into the DMA single cantilever while strain was measured during a constant stress ramp from 0-6 N.

Results and Discussion

The inclusion of N-vinyl pyrrolidinone (NVP) is well known to increase polymerization rate in acrylate photopolymerization in the presence of oxygen. To focus on the unique properties of the copolymerization of NVP and acrylate, Figure 2 compares the polymerization rate profiles of the neat polymerization of HA, NVP and DPPA to 1:1 molar mixtures of HA/NVP, DPPA/HA and DPPA/NVP. A number of observations can be made when comparing the rate behavior of these systems. First, it is clear that the neat polymerization of NVP is the slowest, exhibiting autoacceleration at moderate conversion before reaching a maximum rate at around 50% conversion. The homopolymerization of hexyl acrylate rises to a maximum rate somewhat greater than NVP at around 3% double bond conversion. Comparing the homopolymerization of these two monomers with the copolymerization of a 1:1 molar mixture of HA/NVP reveals that NVP addition to acrylate monomer serves to significantly enhance polymerization rate. The rate of polymerization for 1:1 HA/NVP is approximately 200% greater than the polymerization rate of HA at 5% double bond conversion.

The increase in rate in HA/NVP copolymerization could be due to the reactivity of the NVP radical. The reported literature value for reactivity ratios for NVP and butyl acrylate (r_1 of 0.02, r_2 of 0.8, M_1 NVP, M_2 butyl acrylate)¹³ indicate that acrylate/NVP copolymerization is predominately alternating (i.e. $r_1 \times r_2$ is approximately zero). The rate enhancement in 1:1 HA/NVP copolymerization therefore infers that cross propagation of NVP and acrylate monomer is very favorable and a significant source of the increased polymerization rate in NVP/acrylate copolymerization.

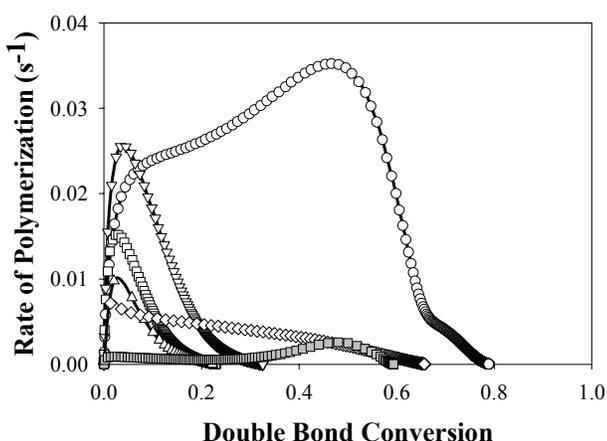


Figure 2. Rate of polymerization versus double bond conversion for photopolymerization of neat NVP (■), neat HA (◇), neat DPPA (△), 1:1 molar DPPA/HA (□), 1:1 molar DPPA/NVP (▽) and 1:1 molar HA/NVP (○).

Similar rate enhancement is seen in copolymerization of NVP with the pentafunctional acrylate DPPA. As shown in Figure 2, the neat polymerization of DPPA exhibits a rapid rise to a maximum rate at less than 3% double bond conversion. Adding both hexyl acrylate and NVP to DPPA result in marked increase in polymerization rate. 1:1 molar DPPA/HA is nearly 150% faster than the neat polymerization of DPPA while 1:1 molar DPPA/NVP is nearly 250% faster than neat DPPA. NVP also increases overall conversion by nearly 10% in comparison to neat DPPA. Adding HA to DPPA reduces the average monomer functionality which is well known to increase polymerization rate in acrylates. DPPA polymerization rate is enhanced to an even greater extent when NVP is added. In addition to reducing the effective monomer functionality of the

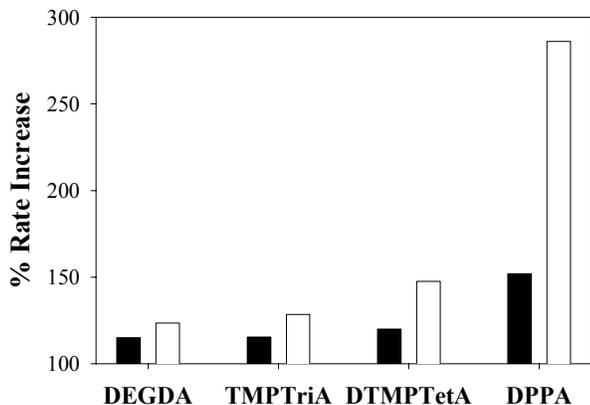


Figure 3. Percent rate increase associated with 15 mol% (■) and 30 mol% (□) NVP in copolymerization with DEGDA, TMPTriA, DTMP TetA and DPPA.

DPPA systems, DPPA/NVP copolymerization rate is enhanced by the favorable cross propagation amongst NVP and acrylate monomer, similar to HA/NVP.

A summary of the maximum polymerization rate for a number of NVP/acrylate formulations is shown in Figure 3. In general, adding NVP increases polymerization rate in comparison to the neat polymerization of the particular system. The influence of NVP on polymerization rate increases with both NVP concentration and monomer functionality. While 30 mol% NVP results in 125% rate increase in DEGDA, it results in a nearly 300% rate increase in DPPA. The behavior of NVP with high functionality acrylates merits further study to determine the means by which NVP enhances photopolymerization of these commonly used monomers.

The influence of NVP in DPPA copolymerization is not limited to polymerization rate. Shown in Figure 4a is RTIR determination of acrylate double bond conversion at 810 cm^{-1} for copolymerizations of DPPA over a wide range of NVP concentrations. Increasing NVP concentration significantly increases acrylate double bond conversion. Acrylate conversion increases from 30% to 80% as NVP concentration is increased from 10 mol% to 90 mol%. Similar to the study of NVP

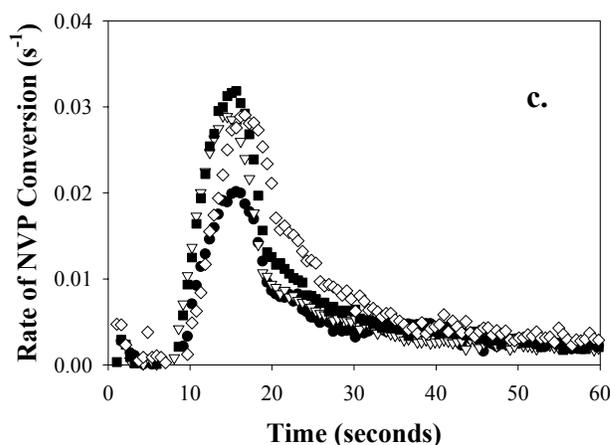
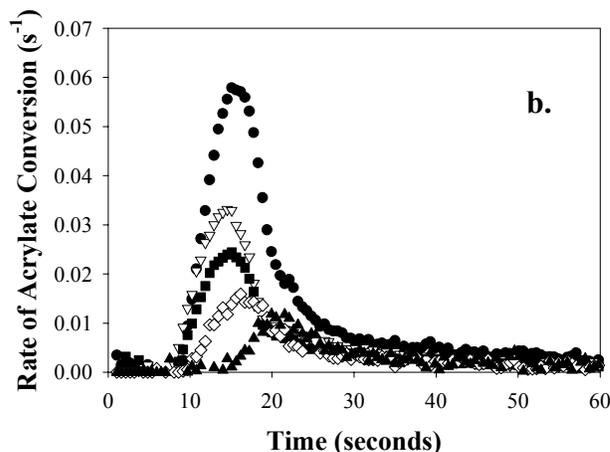
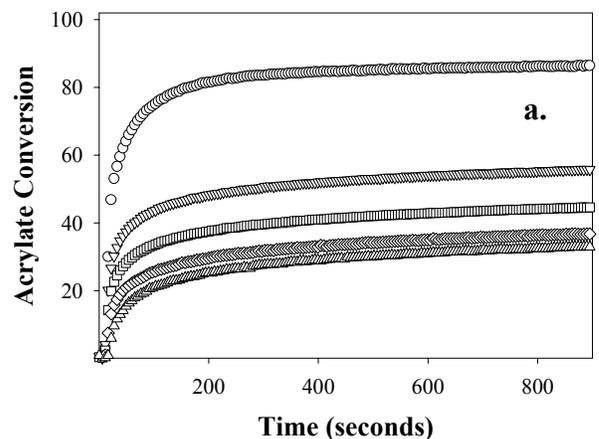


Figure 4. (a) Acrylate conversion as a function of time in copolymerization of DPPA with 90 mol% NVP (○), 70 mol% NVP (▽), 50 mol% NVP (□), 30 mol% NVP (◇) and 10 mol % NVP (△). (b) Rate of acrylate conversion versus time and (c) rate of NVP conversion versus time for copolymerization of DPPA and 90 mol% NVP (●), 70 mol% NVP (▽), 50 mol% NVP (■), 30 mol% NVP (◇) and 10 mol % NVP (▲). The concentration of 10 mol% NVP was insufficient to enable rate determination in Figure 4c.

in HPDLCs, NVP and acrylate conversion are coupled in the polymerization of DPPA.¹⁴

RTIR is also useful in studying polymerization rate for each monomer species. Plotted in Figure 4b is the rate of acrylate conversion versus time for copolymerization of 10-90 mol% NVP and DPPA. As NVP concentration increases, the rate of acrylate conversion increases by nearly 500%. Interestingly, as shown in Figure 4c, a plot of the rate of NVP conversion versus time shows a maximum rate at around 50 mol% NVP. While concentrations greater than 50 mol% NVP continue to increase the rate of acrylate conversion (Figure 4b) it results in decreased rate of NVP conversion. Examination of the overall rate of polymerization by PDSC for these same samples (not shown here) shows a maximum overall rate at around 70 mol%.

Similar to DPPA/NVP polymerization in the HPDLC system, NVP also increases polymerization rate and acrylate monomer conversion in monomer systems without LC. The double bond conversion of DPPA is limited by the highly crosslinked and subsequently quickly vitrified polymerization of this monomer. As noted in Figure 4a, upon complete conversion of NVP, very little additional acrylate conversion occurs. In light of previous study of reaction diffusion termination in acrylate systems¹⁵⁻¹⁷ and similar to the copolymerization of NVP and DPPA in HPDLCs, we propose that the source of coupled conversion of NVP and DPPA is reaction diffusion. In general, reaction diffusion is a bimolecular termination mechanism that occurs when standard segmental or diffusion based termination processes are impossible. Often in vitrified polymers, the only means for trapped radicals to terminate is by propagation through local, unreacted double bonds. Therefore, reaction diffusion termination can be thought of as coupled propagation and termination. The quantity, $R_p^2/[M]$ has been described as an indicator of reaction diffusion termination when it is proportional to the kinetic rate parameter for propagation, k_p . Figure 5 plots $R_p^2/[M]$ versus double bond conversion for 0-30 mol% NVP in DPPA. The kinetic parameter k_p is not plotted here, but is proportional to $R_p^2/[M]$ after the maxima of each curve. Adding NVP shifts the maximum of $R_p^2/[M]$ from 1.4% conversion to as high as 3.6% conversion. Adding minor quantities of NVP shifts the onset of reaction diffusion termination into later double bond conversion. The increase in conversion with NVP concentration is correlated to NVP enabling reaction diffusion termination at double bond conversion greater than 20%. NVP, through its preferential reactivity with acrylate monomer, likely diffuses into the crosslinked polymer network and acts as a bridging agent enabling once-trapped radicals to continue polymerization through reaction diffusion.

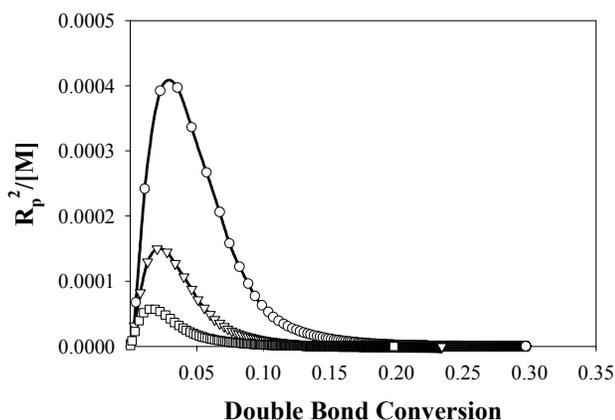


Figure 5. Examination of reaction diffusion termination in DPPA/NVP copolymerization. $R_p^2/[M]$ is plotted against double bond conversion for neat DPPA (\square), 15 mol% NVP in DPPA (∇) and 30 mol% in DPPA (\diamond).

Maintaining the thermal and mechanical properties of acrylate photopolymer is often a critical design criterion in formulation chemistry. To this end, the mechanical and thermal properties of NVP/DPPA systems were studied. As shown in Figure 6, Young's Modulus was determined with DMA for neat NVP, 45 mol% NVP in DPPA, 30 mol% NVP in DPPA, 15 mol% NVP in DPPA and neat DPPA. Interestingly, adding NVP does not alter the mechanical properties of DPPA systems. Neat NVP, with a modulus of 1.2 mPa, might be expected to 'dilute' the modulus in DPPA systems starting at a value around 8.9 mPa.

However, the influence of NVP on acrylate conversion serves to offset the expected decreased

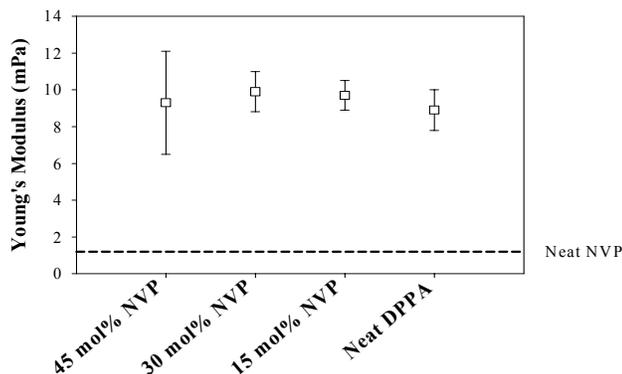


Figure 6. Young's modulus as a function of NVP concentration in copolymerization with DPPA. Dashed line indicates modulus of neat NVP.

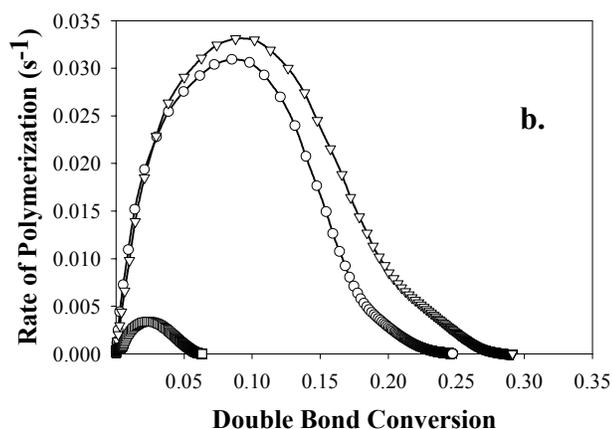
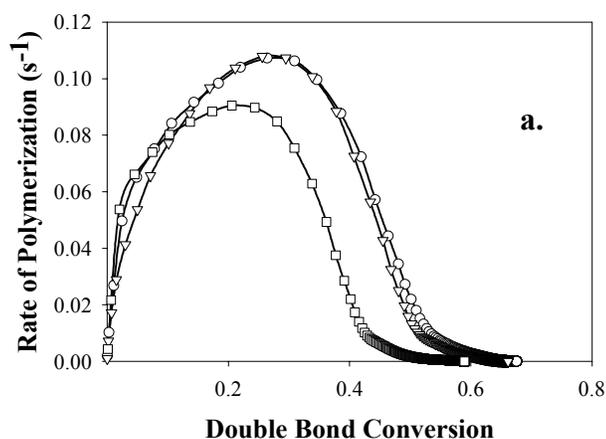


Figure 7. Rate of polymerization versus double bond conversion for neat DEGDA (\square), 30 mol% NVP in DEGDA (\diamond) and 30 mol% NVC in DEGDA (∇) in (a) nitrogen and (b) air.

mechanical properties with NVP incorporation. Though not shown here, NVP is also minimally influential on thermogravimetric analysis of these same copolymers. The evolution of mass loss for DPPA/NVP copolymers is nearly identical as a function of temperature, with significant mass loss beginning at 400° C and the polymer degradation complete at around 600° C.

Including NVP enhances acrylate polymerization by increasing rate and conversion without influencing mechanical or thermal properties to any degree. Unfortunately, NVP has been recently classified as a stage three carcinogen by the International Agency for Research on Cancer.¹⁸ In light of these concerns, industrial formulation chemists have begun to substitute N-vinyl caprolactam (NVC)¹⁹ for NVP in polymer systems. Shown in Figure 7a are the copolymerization of 30 mol% NVP and 30 mol% NVC with DEGDA. Both NVP and NVC increase polymerization rate by 120% in comparison to the neat polymerization of DEGDA. NVC and NVP also exhibit similar behavior in oxygen rich environments. Figure 7b plots the rate of polymerization versus conversion for polymerizations of DEGDA, NVP and NVC in air. As is typical, the neat polymerization of DEGDA is limited to a maximum rate of 0.005 and conversion of just over 5%. The polymerization of 30 mol% NVC in DEGDA is approximately nine times greater than the neat polymerization of DEGDA in air. Once again, the copolymerization of DEGDA/NVC is very similar to the influence of DEGDA/NVP. In comparison to Figure 7a, DEGDA/NVC decreases by nearly 70%.

Conclusion

This work describes the unique characteristics of NVP copolymerization with highly functional acrylate monomer. NVP significantly increases polymerization rate in copolymerization with acrylates of functionality one to five. As the acrylate functionality increases, the percent rate increase jumps from only 125% in the polymerization of 30 mol% NVP and DEGDA to nearly 300% in the polymerization of 30 mol% NVP and the pentaacrylate

DPPA. Increasing NVP concentration also increases acrylate conversion. The copolymerization of NVP and DPPA shows interesting rate behavior. While the polymerization rate for acrylate monomer steadily increases with NVP concentration, NVP polymerization rate has a maximum at around 50 mol% NVP. NVP delays the onset of reaction diffusion in highly crosslinked systems and facilitates greater acrylate conversion through enabling further reaction of acrylate double bonds through reaction diffusion at high double bond conversion. Interestingly, NVP does not alter the Young's modulus of DPPA/NVP copolymers. NVC, a potentially useful alternative to NVP, exhibits virtually identical behavior to NVP in copolymerization in nitrogen and air.

References

- (1) Fouassier, J.-P. *Photoinitiation, Photopolymerization and Photocuring: Fundamentals and Applications*; Hanser/Gardner: Cincinnati, 1995.
- (2) Gou, L., Coretsopoulos, C., Scranton, A.B. *Journal of Polymer Science: Part A: Polymer Chemistry* **2004**, *44*, 1285.
- (3) Gou, L., Opheim, B., Coretsopoulos, C., Scranton, A.B. *Chemical Engineering Communications* **2006**, *193*, 620.
- (4) Decker, C. *Makromolekulare Chemie* **1979**, *180*, 2027.
- (5) Lorenz, D. H., Azorlosa, J.L., Tu, R.S. *Radiat. Phys. Chem.* **1977**, *9*, 843.
- (6) Nicolson, P. C., Vogt, J. *Biomaterials* **2001**, *22*, 3273.
- (7) Lai, Y.-C. *Journal of Applied Polymer Science* **1997**, *66*, 1475.
- (8) Lai, Y.-C. *Journal of Polymer Science: Part A: Polymer Chemistry* **1997**, *35*, 1039.
- (9) Miller, C. W., Jonsson, S., Hoyle, C.E., Yang, D., Kuang, W.F., Kess, R., Iijima, T., Nason, C., Ng, L-T. *Radtech 2000 Technical Proceedings* **2000**, 754-772.
- (10) Miller, C. W., Hoyle, C.E., Jonsson, S., Nason, C., Lee, T.Y., Kuang, W.F., and Viswanathan, K. *ACS Symposium Series # 2003*, 847 (*Photoinitiated Polymerization*).
- (11) White, T. J., Liechty, W.B., Natarajan, L.V., Tondiglia, V.P., Bunning, T.J., Guymon, C.A. *Polymer* **2006**, *In press*.
- (12) Lovell, L. G., Berchtold, K.A., Elliott, J.E., Lu, H., Bowman, C.N. *Polymers for Advanced Technology* **2001**, *12*, 335.
- (13) Al-Issa, M. A., Davis, T.P., Huglin, M.B., and Yip, D.C.F. *Polymer* **1985**, *26*, 1829.
- (14) White, T.J.; Liechty, B.L.; Guymon, C.A. In preparation.
- (15) Anseth, K. S., Wang, C.M., and Bowman, C. N. *Macromolecules* **1994**, *27*, 650-655.
- (16) Anseth, K. S., Kline, L.N., Walker, T.A., Anderson, K.J., and Bowman, C.N. *Macromolecules* **1995**, *28*, 2491-2499.
- (17) Anseth, K. S., Decker, C., and Bowman, C.N. *Macromolecules* **1995**, *28*, 4040-4043.
- (18) *IARC Monographs* **1999**, 71.
- (19) Jansen, J. F. G. A., Houben, E.E.J.E, Tummers, P.H.G., Wienke, D. and Hoffmann, J. *Macromolecules* **2004**, *37*, 2275-2286.