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Acrylic Copolymers Crosslinked by Click Chemistry: Some Aspects of Synthesis, Curing, and Crosslinking

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ABSTRACT: Acrylic polymers bearing pendant azide and propargyl groups were synthesized by chemical transformation of epoxy- and carboxylic functional acrylic precursor polymers and were characterized. These copolymers were crosslinked by reacting them in the presence of Cu(I) catalyst via the azide–alkyne click reaction leading to triazole networks. Influence of catalyst concentration on the crosslinking cure kinetics was investigated, and the activation parameters were evaluated. The activation energy decreased from 90 kJ mol^{-1} to 25 kJ mol^{-1} on catalyzing the cure reaction as estimated by Ozawa method. Differential scanning calorimetric analysis indicated thermal decomposition of the residual azide groups at around 200–220°C, which was catalyzed by Cu(I) with associated activation energy of 130–94 kJ mol^{-1}. Isothermal cure reaction and decomposition of the azide groups were predicted using these parameters. Estimation of crosslink density by solvent swelling and dynamic mechanical analyses showed a normal crosslinking behavior. While the solvent swelling rate and the equilibrium swelling decreased, the front factor and diffusion coefficient of swelling showed a transition from non-Fickian to Fickian as the triazole concentration increased in the network. The click reaction offered an alternate means to crosslink acrylate polymers. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1289–1300, 2013

KEYWORDS: addition polymerization; click chemistry; copolymers; crosslinking

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INTRODUCTION

The acrylic polymers are widely used in textile and paint industry and as cement modifiers, pressure sensitive adhesives, sealants, coatings, etc. The physical properties of the acrylics such as gloss, hardness, adhesion, and flexibility can be modified by altering the composition of the monomer and by the way of controlling their crosslinking. Their crosslinking that consolidates the coating or adhesive is generally done by using peroxides, UV radiation or through reaction of specific reactive groups such as epoxy, amine, phenol, and COOH present in the polymer. Thus, acrylic coating systems comprising blends of ammonium salts of acrylic acid (AA)–acrylic ester copolymers were crosslinked by reaction of pendant ester groups with alkoxymethylmelamine.[1] Acrylates with pendant carboxylic acid groups were crosslinked with metal complexes to obtain acrylic self-adhesives.[2] In certain cases, crosslinking is done through chelation of the carboxylic acid groups through polyvalent metal ions.[3] Use of polyfunctional acrylic, polyacrylate-distyrenic monomers in the presence of free radical initiators for crosslinking is a widely accepted practice.[4,5] Acrylic film adhesives bearing pendant phenol and epoxy groups crosslinked by the amine-epoxy and phenol-epoxy reactions have been reported by us.[6,7] With a view to explore click chemistry for crosslinking acrylate polymers, the present work was undertaken. "Click reaction" involving 1,3-dipolar cycloaddition (Huisgen reaction) between azide and alkyne groups has been reported as a fast and nearly quantitative reaction and is used as a tool for building diverse molecular architecture.[8–10] However, this chemistry has hardly been explored for crosslinking acrylic polymers. Sumerlin et al. reported the direct atom transfer radical polymerization (ATRP) of 3-azidopropyl methacrylate and the functionalization of the corresponding polymers in the presence of mono-substituted alkynes.[11] A direct reversible addition-fragmentation chain transfer polymerization of azido alkyl methacrylate and its subsequent click reaction with phenyl acetylene has been described.[12] Mespouille et al. reported the synthesis of amphiphilic and environmental responsive polymer networks by click chemistry.[13] Matyjaszewski and coworkers reported the ATRP of glycidyl methacrylate (GMA) followed by ring-opening of the oxirane rings by sodium azide and the Cu(I)-catalyzed cycloaddition of the resultant polymer with poly(ethylene oxide) methyl ether 4-pentynoate leading to loosely grafted copolymers.[14] A combination of ATRP of 1-ethoxyethyl acrylate and the copper(I)-catalyzed "click" reaction of azides and terminal alkynes was evaluated as a method to synthesize diverse amphiphilic copolymer structures.[15] Synthesis

of poly(oxazoline)–poly(siloxane)–poly(oxazoline) block copolymers has been realized by clicking together the segments.[16] The azide−alkyne cycloaddition has also been utilized for the synthesis of well-defined acylated polymers with perylenebisimide[17] or mannose units.[18] Star polymers were realized using the click reaction between an azide-end-functionalized polystyrene, poly (*tert*-butyl acrylate), or poly(ethylene glycol) precursor and a tris alkyne-functional initiator.[19] Pascault and coworkers reported copper-catalyzed step growth click polymerization of α-azide–ω-alkyne dianhydrohexitol stereoisomers[20] and high T_g bio-sourced networks by performing the reaction in the presence of a tailor-made symmetrical crosslinker.[21] The versatility of click reaction for polymer synthesis has been exemplified in many reports and review articles.[22–25]

In this article, we report the application of click chemistry for crosslinking acrylic polymers. For this, azide- and alkyne-functionalized acrylate polymers were synthesized by free radical polymerization technique followed by chemical transformation. These polymers were subsequently crosslinked via click reaction. Apart from synthesis and characterization and curing of these polymers, their crosslinking and associated solvent swelling studies have also been reported. Though click chemistry has been well explored for the synthesis of pendent and end-functional polymers, graft, block copolymers, etc., it has not been much used for effective crosslinking of addition polymers. The novelty of this work lies in exploring the well-known click reaction for crosslinking of acrylate polymers.

EXPERIMENTAL

Materials and Methods

The monomers, butyl acrylate (BuA, 99%), AA (99%), and GMA (97%), were obtained from Alfa Aesar (UK). The polymerization inhibitor was removed from BuA by passing the monomer through a column filled with basic alumina. AA and GMA were vacuum distilled at 80°C. Propargyl bromide (80%, w/w, in toluene) was procured from Alfa Aesar and was used as such. Sodium azide, ammonium chloride (Qualigens, Mumbai), and cuprous iodide (98%, Aldrich, USA) were also used as such. Tetrahydrofuran (THF) and methyl ethyl ketone (MEK; 99%, Qualigens, Mumbai) were dried over molecular sieves (4Å) prior to use.

Fourier Transform Infrared Spectroscopy. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Perkin-Elmer spectrum GXA model, in the range of 4000–550 cm^{-1} with a resolution of 4 cm^{-1}.

^{1}H Nuclear Magnetic Resonance Spectroscopy. ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR) spectra were recorded with a Bruker Avance NMR spectrometer (300 MHz) in deuterated acetone.

Gel Permeation Chromatography. The gel permeation chromatographic (GPC) analysis was carried out with Waters Alliance 2690 separation module in conjunction with Waters 410 differential refractive index detectors. Waters HR1 and HR2 AQ 5 Styragel columns were used for separation.

Differential Scanning Calorimetry and Thermogravimetric Analysis. Differential scanning calorimetry (DSC) was carried out using a Mettler DSC Q20. The samples were heated from ambient to 300°C at varying heating rates ranging from 3 to 10°C min^{-1} in N_2 atmosphere; thermogravimetric analyses (TGAs) were done from room temperature (RT) to 600°C at a heating rate of 10°C min^{-1} in N_2 atmosphere using a TA instrument Q600.

Dynamic Mechanical Thermal Analysis. Dynamic mechanical properties were determined using TA instrument Q800 with a frequency of 1 Hz at a ramp of 3°C min^{-1} in tension mode.

Synthesis of Poly(BuA-co-AA). BuA (100 g, 0.78 mol), AA (6.23 g, 0.086 mol), MEK (100 mL), and azobisisobutyronitrile (AIBN) (0.25 wt % total monomer) were mixed in a reactor and polymerized at 70°C under inert atmosphere for a period of 6 h. The reaction was quenched, and the contents were diluted with THF. The polymer was then precipitated in to a large volume of cold methanol–water mixture (80 : 20 by volume). The precipitated polymer was dissolved in THF and reprecipitated thrice as above so as to remove the unreacted monomer and left out initiator. The product was dried under reduced pressure at 60°C for 16 h to get the polymer with a yield of 80%. The product was characterized by acid value. Acid value of 46 implied that the polymer contained 10 mol % of AA. GPC analysis showed $M_n = 30{,}500$ g mol^{-1} and $M_w/M_n = 5.2$.

Synthesis of Poly(BuA-co-propargyl acrylate). A solution of 10 g of the above poly(BuA-co-AA) in 60 mL MEK was introduced to a round bottom flask equipped with a stirrer. Dried potassium carbonate (0.55 g) and a trace of phase transfer catalyst (benzyl triethyl ammonium chloride) were added to this solution. Propargyl bromide (1.2 g of 80% solution) was added, and the mixture was refluxed for 24 h. The precipitate was filtered off, and the filtrate was poured into 0.1*N* HCl in cold water to get a tacky polymer that was washed twice with water. The polymer was purified by reprecipitation of its solution into water. The precipitate was dissolved in dichloromethane and dried over anhydrous sodium sulfate, and the solvent was removed by flash evaporation. The residue was dried at 50°C for 8 h under reduced pressure (yield, 70%). GPC: $M_n = 58{,}800$ g mol^{-1}, $M_w/M_n = 3.3$. FTIR (NaCl): 3266 cm^{-1} (≡C–H), 2341 cm^{-1} (–C≡C–).

^{1}H NMR [300 MHz, D_6 acetone] δ ppm: 4.70 (CH≡C$\underline{CH_2}$O), 2.8 ($\underline{CH}$≡C), 2.2 (–$\underline{CH}$COO), 1.9 ($\underline{CH_2}$–CHCOO) all of propargyl acrylate: 0.92 (–CH_3), 1.40 (–CH_2 –CH_2–$\underline{CH_2}$–CH_3), 1.60 (–CH_2 –$\underline{CH_2}$–CH_2–CH_3), 1.9 ($\underline{CH_2}$–CHCOO), 2.33 (–$\underline{CH}$–COO), 4.1 (–COO$\underline{CH_2}$–) all of BuA. Acid value: nil.

Ratio of protons –COO$\underline{CH_2}$– in BuA : propargyl acrylate was 10 : 1.

Synthesis of Poly(BuA-co-GMA). BuA (100 g, 0.78 mol) and GMA (12.3 g, 0.087 mol) were added to 200 mL MEK in a polymerization reactor under inert atmosphere. Polymerization was initiated at 70°C by adding 0.57 g of AIBN. After 6 h, the reaction was stopped by diluting with THF. The copolymer was recovered by precipitation of the solution in cold methanol–water mixture (80 : 20 by volume) followed by dissolution in THF and reprecipitation as above. Drying was done under

reduced pressure at 60°C for 8 h (yield, 80%).The product contains nearly 10 mol % of GMA, as determined by epoxy content (0.9 eq kg^{-1}) and ^1H NMR. GPC: ($M_n = 52{,}700$ g mol^{-1}, $M_w/M_n = 5.2$). FTIR: 907 cm^{-1} (epoxy ring str), 1732 cm^{-1} (C=O str).

^1H NMR (300 MHz, $CDCl_3$) δ ppm: Polyglycidyl methacrylate (PGMA): 4.27 (COO$\underline{CH_2}$), 3.78 (—$\underline{CH_2}$–$\underline{CH}$(O)–$\underline{CH_2}$), 3.20, 2.81 (COO–$\underline{CH_2}$–$\underline{CH}$(O)–$\underline{CH_2}$), 2.60 ($\underline{CH}$–COO), 1.86 (–$\underline{CH_2}$–CH–), 1.0 (–$\underline{CH_3}$), BuA 0.90 (–$\underline{CH_3}$), 1.40 (–CH_2 –CH_2–$\underline{CH_2}$–CH_3), 1.50 (–CH_2 –$\underline{CH_2}$–CH_2–CH_3), 1.8($\underline{CH_2}$–CHCOO), 2.30 (–$\underline{CH}$–COO), 4.0 (–COO$\underline{CH_2}$–). Proton ratio of COO$\underline{CH_2}$ in BuA and GMA implied mole fraction of GMA is 0.1.

Synthesis of Poly(BuA-co-azido hydroxypropyl methacrylate). To a solution of the above copolymer of BuA and GMA (0.07 g) in 10 mL DMF, sodium azide (0.1 g) and ammonium chloride (0.50 g) were added, and the mixture was stirred at 50°C for 24 h. The polymer containing azido hydroxypropyl methacrylate units was precipitated in water. The polymer was reprecipitated into water after dissolving in THF (two times) and dried. GPC: $M_n = 69{,}700$ g mol^{-1}, $M_w/M_n = 4.2$. FTIR: 2104 cm^{-1} ($-N_3$), 3508 cm^{-1} (OH). ^1H NMR (300 MHz, D_6 acetone): BuA 0.90 (–CH_3), 1.40 ppm (–CH_2 –CH_2–$\underline{CH_2}$–CH_3), 1.50 ppm (–CH_2–$\underline{CH_2}$–CH_2–CH_3), 1.8 ppm ($\underline{CH_2}$–CHCOO), 2.30 ppm (–$\underline{CH}$–COO), 4.0 ppm (–COO$\underline{CH_2}$–). Azido hydroxypropyl methacrylate: 3.5 ppm (–$\underline{CH_2}$–N_3), 3.9 ppm (–$\underline{CH}$OH–), 4.1 ppm (CO–$\underline{CH_2}$– merged with BuA part). Ratio of –COO$\underline{CH_2}$– and –$\underline{CH_2}$–N_3 (BuA : azidopropyl methacrylate) is 10 : 1.

Synthesis of Bisphenol A Bis(azido hyroxypropyl) Ether. Bisphenol A bis(azido hyroxypropyl) ether (BABA) was synthesized as per Scheme 4. Bisphenol A diglycidyl ether (20.4 g), sodium azide (5.85 g), ammonium chloride (4.0 g), and 100 mL DMF were introduced into a 250 mL round bottom flask. The reaction flask was covered with dark cloth and kept at room temperature for 2 days and at 50°C for 1 day. The reaction mixture was poured into water; the product was extracted with diethyl ether and washed several times with water. The diethyl ether was evaporated off, and the product was dried under vacuum at room temperature for 16 h. The bisazide product was characterized by spectroscopy techniques. The product consists of isomers of bisazido propyl ether of bisphenol A.

^1H NMR (major isomer-bis-3-azido-2-hydroxypropyl ether of bisphenol A, 300 MHz, D_6 acetone): $\delta = 1.63$ (s, 6H, CH_3), 3.5 (m, 4H, CH_2–N_3), 4.00 (d, 4H, O–CH_2), 4.2 (m, 2H, CH–O**H**), 6.80–7.10 (8H, –Ar). FTIR (KBr, cm^{-1}): 2102 (azide), 3379 (–OH).

Crosslinking of the Polymers. The azide containing polymer was reacted with propargyl functional acrylate polymer in different ratios in the presence of 0.3 wt % of CuI as catalyst at 60°C for 20 h. The molar ratios of azide : propargyl groups in three cases are 100 : 3, 100 : 5, and 100 : 10. The mixing was done by dissolving both the polymers together, along with the catalyst, in acetonitrile followed by casting the mixture as a thin film and heating it at 60°C for 20 h. The cured product was characterized by FTIR. Crosslink density of the film was determined by swelling studies and dynamic mechanical analyses (in typical case). Thermal stability was determined by TGA.

Swelling Experiments. Swelling measurements were done by confining the film in a tea bag.[26–28] About 1 g of the cured sample was left to swell in toluene at ambient temperature. At the beginning of each experiment, the sample was placed on a grid boat made of nylon cloth (with a mesh size of 1 mm) to avoid breakage of the fragile gel and was weighed accurately. The sample along with grid boat was again immersed in the solvent for continuation of swelling. The sample was weighed at regular intervals after gently wiping off the excess solvent with a tissue paper. This was continued until the sample attained constant weight. Toluene was chosen for swelling studies as it is a "good solvent" for acrylates with a solubility parameter of 18.3 $MPa^{1/2}$ close to that of acrylates (18.4 $MPa^{1/2}$) in general. Toluene has been used for such polymer systems.[29,30]

RESULTS AND DISCUSSION

Poly(BuA-co-propargyl acrylate) was synthesized from poly (BuA-co-AA) by reacting the carboxylic acid with propargyl bromide. The esterification reaction is shown in Scheme 1. From the acid value of the precursor and of the derivative, the polymer was estimated to contain 10 mol % propargyl acrylate and 90% BuA. Lack of residual acid in the propargyl derivative confirmed that the esterification reaction was complete.

The structure and composition of the propargyl functionalized polymer was further confirmed from spectroscopic analyses. In the FTIR spectrum, the peak at 3266 cm^{-1} due to the ≡$\underline{CH}$ and that at 2341 cm^{-1} corresponding to $\underline{C}\equiv\underline{C}$ were seen [Figure 1(b)]. From the integration of the signals at 4.7 ppm (—OOC—$\underline{H_2C}$—C≡)-COOCH2-C≡CH and 4.1 ppm (–COO$\underline{CH_2}$–), the composition was calculated as 10 : 1 (BuA : propargyl acrylate).

GPC analysis implied an apparent increase in molecular weight of the polymer on esterification (M_n increased from 33,000 to 58,800). The disproportionate increase can be a consequence of the increased hydrodynamic volume of the fully esterified polymer *vis-à-vis* the precursor containing 10 mol % of carboxylic acid.

The azide containing acrylate polymer was synthesized from the copolymer of BuA and GMA by reaction with NaN_3 as shown in Scheme 2. NaN_3 opens up the epoxy groups to generate azido hydroxyalkyl groups. Earlier synthesis of azide functional acrylates was based on the controlled radical polymerization of azido acrylate monomers.[12,31,32] In the present work, a combination of conventional free radical polymerization and chemical transformation was adapted for synthesizing the azido acrylate polymer. The precursor polymer contained 10 mol % of glycidyl units as inferred from the NMR data and epoxy value. After conversion, no residual epoxy group was observed, implying that the epoxy groups were completely transformed to azido derivative. This was ascertained also from the nitrogen content (experimental 3.0% and theoretical 3.1%) of the resulting polymer. The azide groups were detected in infra red (IR) spectrum [Figure 1(a)] at 2104 cm^{-1} at the cost of the epoxy rings whose absorption at 907 cm^{-1} disappeared from the spectrum of precursor polymer. Appearance of OH bond at 3400 cm^{-1} further

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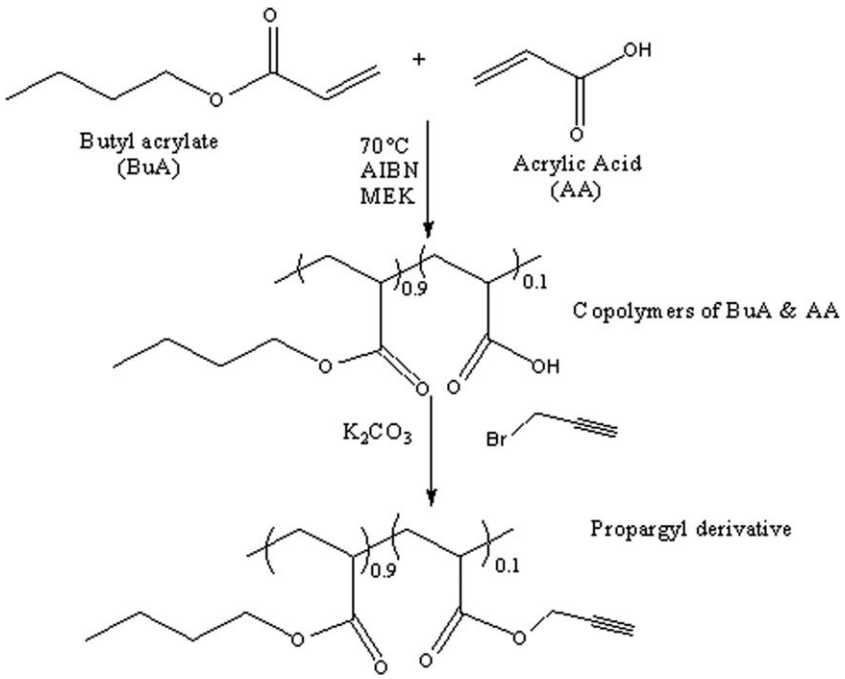


Scheme 1. Synthesis of poly(BuA-co-propargyl acrylate).

substantiated the ring-opening. The azido substitution was further confirmed from NMR analysis. From a comparison of the relative intensities of signals corresponding to $COO–CH_2–$ (of BuA units) and $CH_2–N_3$, the polymer was estimated to contain BuA and azido hydroxypropyl methacrylate in molar ratio 10 : 1. GPC analyses showed that the molecular weight of the azide derivative ($M_n = 69{,}700$) marginally increased with respect to that of the precursor polymer ($M_n = 58{,}800$).The overall molar mass remains practically unaffected. This is evident from the GPC traces of the two polymers shown in Figure 2. The GPC analysis confirmed lack of any spurious crosslinking or branching during ring-opening reaction.

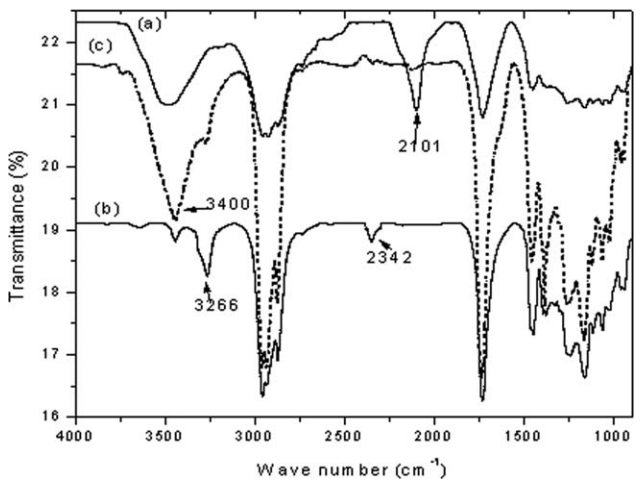


Figure 1. FTIR spectrum of (a) azide derivative, (b) propargyl derivative, and (c) triazole network polymer.

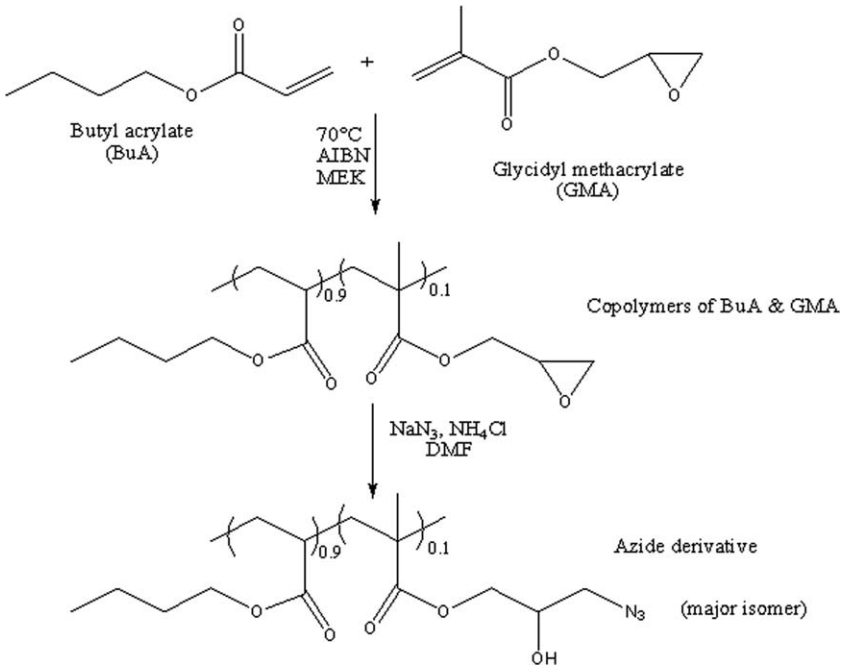
Crosslinking via Click Reaction

The crosslinking was done by mixing the azide and propargyl acrylate polymers and heating them in the presence of copper catalyst. The click reaction of the azide and propargyl functional acrylic polymers in the presence of copper iodide catalyst proceeds as shown in Scheme 3. For swelling studies, crosslinking was limited for which the two polymers were mixed in proportions such that the azide : propargyl ratio was 100 : 3, 100 : 5, and 100 : 10 (molar ratio). This would lead to some residual quantity of unreacted azide groups in the cured polymer. For kinetic studies, the equivalent ratio was maintained as 1 : 1.

The cure reaction was monitored by FTIR spectroscopy. Figure 1(c) shows the FTIR spectrum of the crosslinked polymer. The strong absorption band at 2100 cm^{-1} ascribed to the $–N_3$ group in azide and that at 2338 cm^{-1} due to the propargyl group disappeared completely after the cycloaddition, indicating complete formation of the triazole network. The peak corresponds to the triazole groups that were located in the range 1500–1700 cm^{-1}. Crosslinking was confirmed from the insolubility of the cured polymer in any solvent especially for the molar ratio of 1 : 1.

Cure Kinetics and Catalysis

The curing reaction of azide- and alkyne-functionalized acrylic polymers was monitored using DSC using a 1 : 1 molar mixture of azide and propargyl functional polymers. DSC thermograms of curing of azide and propargyl derivatives with and without catalyst are shown in Figure 3. The non-isothermal DSC showed two exotherms. The first exotherm is attributed to the click reaction. The presence of 0.3% catalyst facilitates lowering of the cure initiation temperature from 120°C to almost 60°C. Data in Table I reveal that cure exotherm systematically shifts to



Scheme 2. Synthesis of poly(BuA-co-azido hydroxypropyl methacrylate).

lower temperatures with increased catalyst concentration for a given heating rate.

The enthalpy of curing was computed from the DSC from the area under the exotherm after accounting for the unreacted part. For this calculation, the heat of decomposition of azide was required, and it was estimated by DSC analysis of a model bisazide, i.e., BABA (discussed later). The heat of decomposition of azide was obtained as 133 kJ mol^{-1}.

The enthalpy of curing amounted to 231.5 kJ mol^{-1}. This value is in good agreement with the value reported by Pascault and coworkers[20] (232 kJ mol^{-1}).

The curing reaction was analyzed using Ozawa method by the following equation[33]:

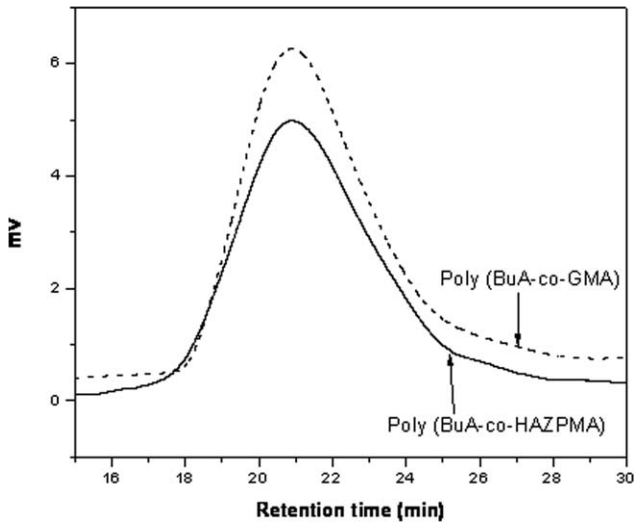


Figure 2. GPC of poly(BuA-co-GMA) copolymer and its azide derivative.

$$\frac{2.15d[\log(\phi)]}{d(1/T)} = \frac{-E}{R} \quad (1)$$

where T is the temperature corresponding to the maximum in the DSC exotherm at a heating rate, ϕ, and R is the gas constant. The DSC peak maxima were determined at three heating rates. The slope of the linear plot of $\log(\phi)$ against $1/T$ gives E/R. The pre-exponential factor A is given by the equation (2):

$$A = \phi E e^{E/RT}/RT^2 \quad (2)$$

where A is the pre-exponential factor, E is the activation energy for the curing reactions, T is the peak of exothermic temperature, R is the gas constant, and ϕ is the heating rate. The order of the cure reaction (n) was calculated using Coats–Redfern equation.[34] The general equation used is

$$\ln\left[g(\alpha)/T^2\right] = \ln\{(AR/\phi E)(1-2RT/E)\} - E/RT \quad (3)$$

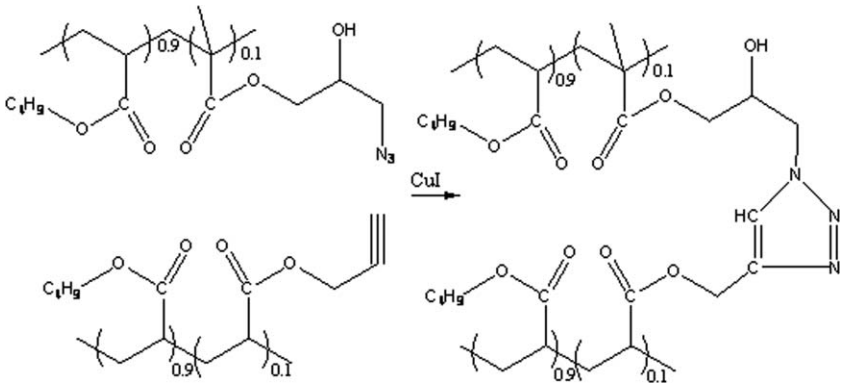
where

$$g(\alpha) = \left\{1-(1-\alpha)^{(1-n)}\right\}/(1-n), \quad \text{for } n \neq 1$$

and when

$$\text{for } n=1,\ g(\alpha) = -\ln(1-\alpha)$$

where A is the pre-exponential factor, α is the conversion, E is the activation energy, n is the reaction order, T is the temperature, Φ is the heating rate, and R is the gas constant. The fractional conversion α is obtained from the cure exotherm, $\alpha = H_\alpha/H_t$, where H_α is the fractional enthalpy at temperature T and H_t the total enthalpy computed from DSC thermogram. A plot of



Scheme 3. Crosslinking via click reaction of poly(BuA-co-propargyl acrylate) and poly(BuA-co-azido hydroxypropyl methacrylate).

$\ln[g(\alpha)/T^2]$ versus $1/T$ at different assumed values of n gave the best linear fit for $n = 2$, this being the order of the reaction.

The activation energies were computed for the uncatalyzed as well as catalyzed systems as per eq. (1). "E" values are considerably lower for the catalyzed system. The variation of E with catalyst concentration is depicted in Figure 4. The activation energy drops from 90 kJ mol^{-1} to nearly 25 kJ mol^{-1} on addition of 0.5% catalyst.

The non-isothermal DSC showed two exotherms. The second exotherm (Figure 3) in DSC is attributed to the decomposition of the unreacted azide groups. The ramping of temperature does not give sufficient time for all the azide–alkyne groups to react despite maintaining a stoichiometric ratio. The origin of the second exotherm was confirmed from the DSC analysis of BABA that was synthesized. BABA was derived from bisphenol A diglycidyl ether by reaction with NaN_3 (Scheme 4). On subjecting it to DSC analysis, it was found out that azide groups in BABA decompose at nearly the same temperature as the azide groups in the polymer blends. The azide decomposition was found to be catalyzed by CuI as seen from the DSC thermogram of BABA in Figure 5, where the exotherm shifts to lower temperature on adding CuI catalyst. Thus, the second exotherm in the DSC of the blend of the polymers was attributed to the decomposition of unreacted azide. In uncatalyzed polymer blend system, the azide decomposition is accompanied by the polymer degradation. Though stoichiometry of azide and alkyne is maintained, during dynamic heating, the reactants do not get enough time to undergo complete reaction. Further, TGA of the azide containing polymer showed a mass loss of about 2% at around 220°C corresponding to the decomposition of azide groups. This is in agreement with the azide content of the polymer (3 wt % azide liberates 2% nitrogen). All these confirmed that the second exotherm in DSC of the blend originated from the decomposition of the azide groups.

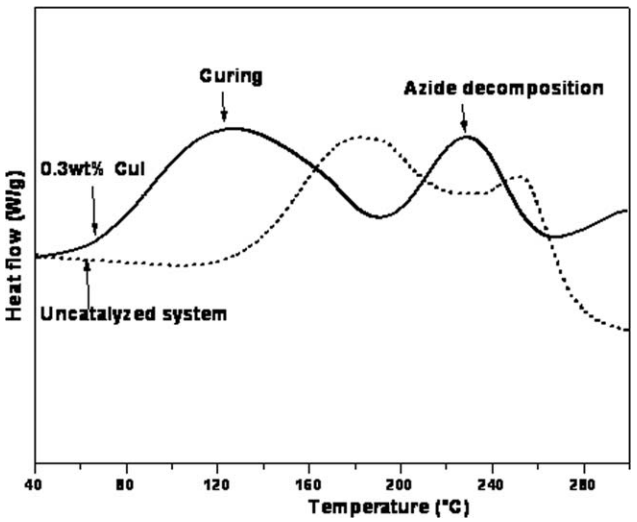


Figure 3. DSC thermogram of curing of azide–propargyl system with and without catalyst.

TGA (Figure 6) of stoichiometrically cured (isothermally at 60°C) polymer confirmed that the cured polymer is quite stable and that the triazole decomposes along with the main polymer backbone at about 340°C. The DTG showed a minute inflection at 220°C due to decomposition of trace amount of unreacted azide groups left in the chain.

The activation energy for the azide decomposition also decreased significantly on catalysis. On adding 0.5% catalyst, the activation energy dropped from 130 kJ mol^{-1} to 93 kJ mol^{-1}. A comparison of the catalysis of cure and decomposition shows that the cure reaction is more sensitive to catalysis than the decomposition (at 0.5% catalyst, activation energy decreases 3.6 times for cure, while it decreases by 1.4 times only for decomposition).

In general, the activation energy varied with catalyst concentration by an empirical relation:

$$E = E_0/(1+bC) \quad (4)$$

where C is the catalyst concentration, b is a constant, and E_0 is the activation energy at 0% catalyst concentration. Value of b is 7.5 $(wt\ \%)^{-1}$ for click cure and 3.1 $(wt\ \%)^{-1}$ for azide decomposition.

The kinetic modeling is generally used for the cure time–temperature prediction of polymer systems. The equation relating time, temperature, and fractional conversion at any time, t, is given as

Table I. DSC Peak Maxima for Cure Reaction and Decomposition of Azide at Varying Catalyst Concentrations for Different Heating Rates

Heating rates (°C min^{-1})	Uncatalyzed Peak maxima (°C)		0.1% catalyst Peak maxima (°C)		0.3% catalyst Peak maxima (°C)		0.5% catalyst Peak maxima (°C)	
	Cure	Decomposition	Cure	Decomposition	Cure	Decomposition	Cure	Decomposition
3	166	232	133	225	114	206	103	202
7	179	245	147	239	127	222	125	220
10	188	251	170	249	159	230	164	228

$$\alpha = 1 - \{1 - A(1-n)te^{(-E/RT)}\}^{1/(1-n)} \quad (5)$$

$$\ln(1-\alpha) = Ae^{(-E/RT)}t, \quad \text{for } n=1 \quad (6)$$

where

$$E = E_0/(1+bC)$$

where α is the fractional conversion, A is the pre-exponential factor, n is the order of reaction, R is the gas constant, t is the time, E is the activation energy, and T is the temperature.

The extent of conversion for cure reaction as well as decomposition of azide under given conditions of temperature, catalyst concentration, and duration was theoretically predicted by using eqs. (5) and (6), respectively. Thermal decomposition generally follows a first-order kinetics, and for isothermal prediction in this case, n was taken as 1. Figure 7 shows the influence of catalytic concentration on cure profile at 60°C. From the data, it is seen that the cure gets completed (~97%) in about 20 h at 60°C at a catalyst concentration of 0.3%. Based on the prediction, this condition was chosen for curing the polymer. To verify this prediction, the polymer heat treated under these conditions (60°C/20 h) was analyzed by DSC. Absence of any exotherm due to residual cure in the temperature range 100–200°C confirmed that curing is completed as per prediction. Prediction for decomposition of azide shown in Figure 8 indicates that significant decomposition of azide groups sets in the presence of 0.3% catalyst at temperatures greater than 140°C.

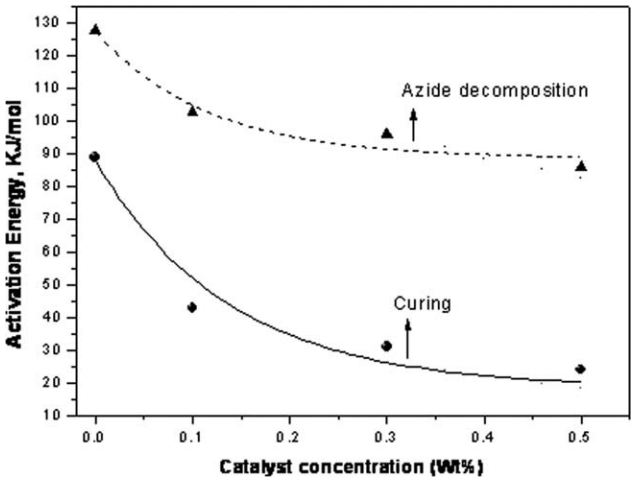


Figure 4. Effect of catalyst concentration on activation energy for cure reaction and azide decomposition.

At 180°C, the decomposition is quite rapid. Isothermal prediction implied that at 180°C, azide decomposes almost completely in about an hour at 0.5 wt % catalyst concentration. In the absence of catalyst, azide groups are quite stable at this temperature. This study shows the need for avoiding metallic impurities in organic azide in order not to risk its decomposition. Catalytic effect on the stability of azides has not been reported before.

Solvent Swelling and Crosslink Density

In order to assess the nature of crosslinking and crosslink density, swelling studies of the cured resin were undertaken. Azide–alkyne ratio was varied to alter the crosslink density of the cured networks, and the swelling indices were determined at different time intervals. For this, the azide polymer was mixed with propargyl polymer in molar ratio of azide : propargyl as 100 : 3, 100 : 5, and 100 : 10 (with respect to the functional group). Toluene was selected as the swelling solvent, as its solubility parameter (18.3 MPa$^{1/2}$) is very close to that (18.4 MPa$^{1/2}$) of the base polymer, i.e., polybutyl acrylate (constituting more than 90% of the composition) to ensure good solvation.

The isothermal degree of swelling (SD), defined as the amount of solvent embedded per unit mass of the polymer, was determined from the relation (7):

$$\mathrm{SD}[\%] = \left(\frac{W_t - W_0}{W_0}\right) \times 100 \quad (7)$$

where W_0 is the initial weight of the dried polymer at $t = 0$, and W_t is the weight of the toluene penetrated into the gel at time t.

Swelling indices for differently crosslinked polymer at varying time intervals are shown in Figure 9.

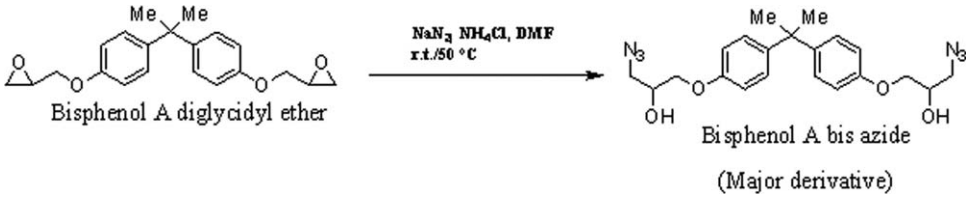
Swelling Kinetics. In order to illustrate the swelling mechanism, the following semi-empirical relation was used. The extent of swelling is given as[35–37]

$$W_t/W_e = kt^n$$

or

$$\ln(W_t/W_e) = \ln(k) + n\ln(t) \quad (8)$$

where W_e is the amount of solvent absorbed at swelling equilibrium, W_t is the amount of solvent absorbed at time t, k is the front factor related to the structure of the polymeric network, and n is the diffusion exponent which indicates the mechanism of swelling phenomena.



Scheme 4. Synthesis of azide derivative of diglycidyl ether bisphenol A.

The value of n usually varies from 0 to 1. For Fickian kinetics, $n = 0.5$ and the swelling is generally known as diffusion controlled, where the rate of solvent penetration is the slowest and hence is the rate determining step. When the solvent penetration velocity and the chain relaxation or chain stretching rates are comparable, n is generally found between 0.5 and 1.0, and the kinetics is generally known as non-Fickian. When the solvent penetration rate is much higher than the chain relaxation rate, then the penetration of solvent is proportional to the time, i.e., $n = 1.0$.

To determine the diffusion exponent (n) and front factor (k), the experimental data were analyzed using eq. (8) as shown typically in Figure 10. From the slope and intercept of the linear plots, n and k were calculated and are compiled in Table II.

The results show that during swelling, the lightly crosslinked polymer indicates higher values of diffusion exponent (n) and swelling rate constant (k). The gel shows a moderate crosslinker concentration-dependent swelling behavior with a transition from non-Fickian ($n = 0.502$) to Fickian ($n = 0.470$), as the concentration of the crosslinking agent increases from 3% to 10%. The present results confirm a good crosslinker sensitivity of swelling.[38] The normalized degree of swelling, Q_t, was calculated:

$$Q_t = (W_s - W_d)/W_d = W_t/W_d \tag{9}$$

where W_s is the weight of the swollen film at time t, W_d is the weight of the polymer at zero time ($t = 0$), and W_t is the weight of the solvent penetrated into the gel at time t. Similarly, the normalized equilibrium degree of swelling, Q_e, is defined as

$$Q_e = (W_\infty - W_d)/W_d = W_e/W_d \tag{10}$$

where W_∞ is the weight of the swollen gel at equilibrium swelling. W_d is the weight of the polymer at $t = 0$, and W_e is the weight of the solvent penetrated into the gel at time t_∞. The normalized equilibrium degree of swelling, Q_e, may be defined as the ratio of amount of toluene transported into the gel matrix at time t_∞ to the initial weight of the polymer sample (at $t = 0$).

Using the values of the normalized degree of swelling at any time t (Q_t) and the normalized equilibrium degree of swelling at t_e (Q_e), it was possible to analyze the kinetic order of the swelling process. For first-order kinetics, the following equation was used[39]:

$$Q_t/Q_e = 1 - e^{-k_n t} \tag{11}$$

$$\ln(1 - Q_t/Q_e) = -k_n t \tag{12}$$

A plot of $\ln(1 - Q_t/Q_e)$ against time t as per eq. (12) gives $-k_n$, as slope. Typical plot is shown in Figure 11, and the calculated rate constants (k_n) are given in Table II.

Data in Table II show that increased crosslinking impedes solvent penetration and diminishes the rate of swelling (k) and equilibrium swelling. However, the normalized swelling rates (k_n) show an apparent increase with increase in crosslink density. This appears so, because k_n denotes the apparent swelling rate (fraction per unit time) under normalized swelling condition. It only means that as the crosslinking increases, the equilibrium swelling diminishes, and the polymer needs less time to attain the attainable equilibrium swelling (which decreases with crosslinking).

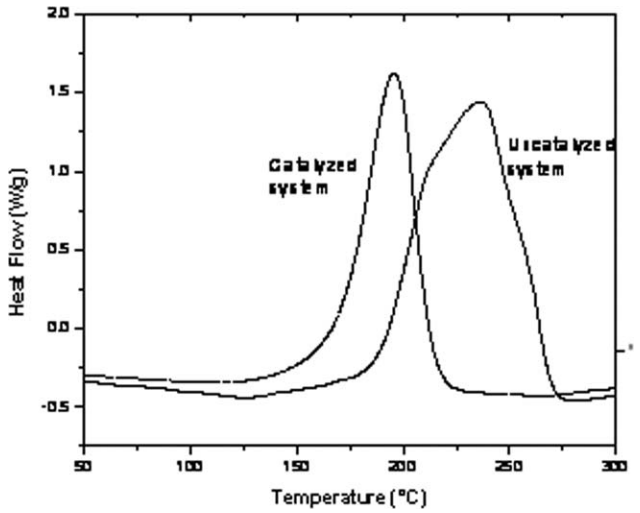


Figure 5. DSC thermogram of azide derivative of diglycidyl ether bisphenol A system with and without catalyst.

Crosslink Density. The number average molecular weight between crosslinks, M_c, can be calculated from the Flory–Rehner equation:

$$-\left[\ln(1 - V_r) + V_r + \chi V_r^2\right] = \rho V_s M_c^{-1}\left(V_r^{1/3} - 0.5 V_r\right) \tag{13}$$

where V_r is the volume fraction of polymer in the swollen gel at equilibrium, χ is the polymer–solvent interaction parameter, V_s is the molar volume of solvent, M_c is the number average molecular weight between crosslinks, and ρ is the density of polymer.

The volume fraction of polymer (V_r) can be calculated from eq. (15):

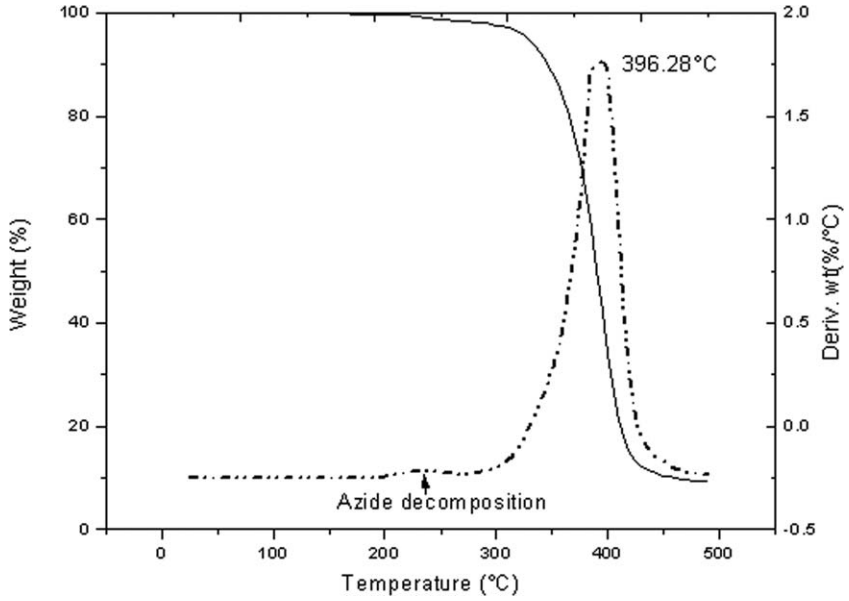


Figure 6. Typical thermogram of cured polymer (1 : 1 azide–propargyl).

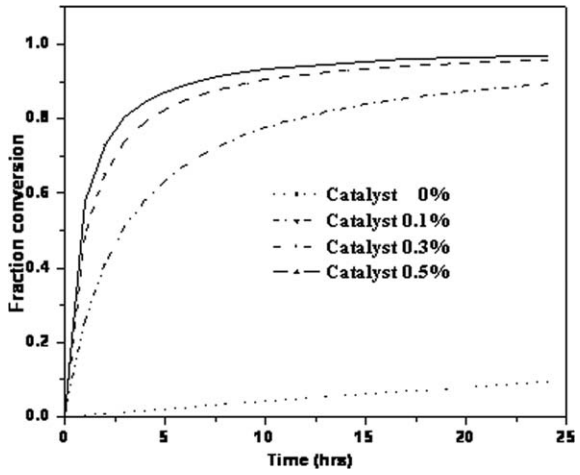


Figure 7. Effect of catalyst concentration on cure conversion at 60°C.

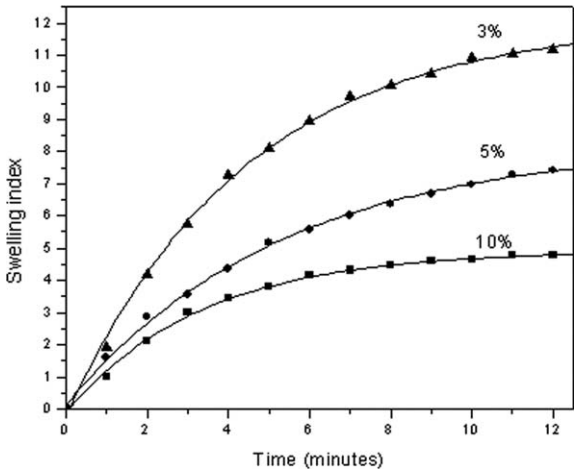


Figure 9. Dependency of swelling index on time for systems crosslinked to different extents.

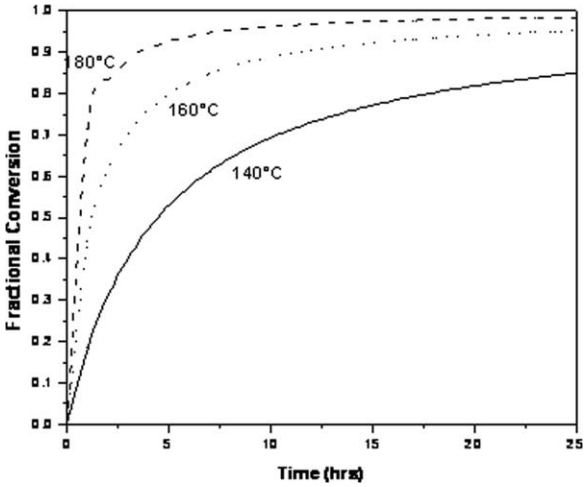


Figure 8. Prediction of isothermal decomposition of azide at 0.3% catalyst concentration at varying temperatures.

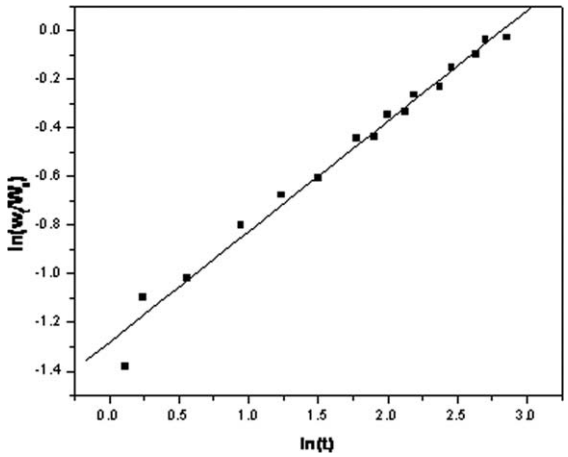


Figure 10. Plot for determination of k and n for system with 3% crosslinker.

Table II. Swelling Kinetic Parameters for Varying Crosslinking

Extent of crosslinking[a] (%)	Diffusion exponent, n	Swelling constant or front factor, k (min^{-n})	Swelling rate, k_n (min^{-1})	Equilibrium swelling (%)
3	0.502	0.393	0.10	1200
5	0.474	0.325	0.22	850
10	0.470	0.279	0.27	450

[a] in terms of molar % of propargyl with respect to azide groups.

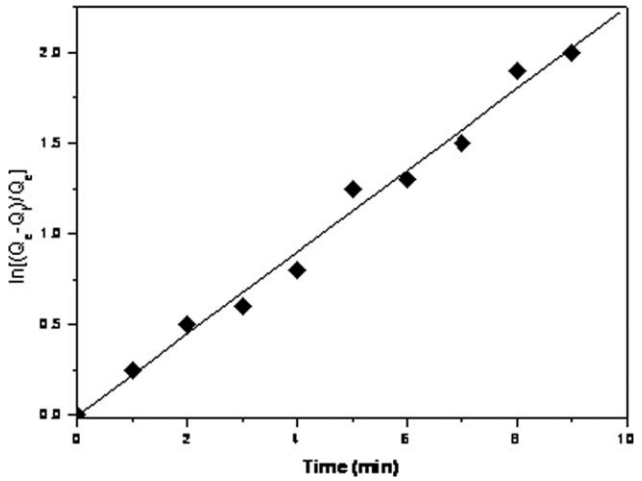


Figure 11. Typical plot for first-order swelling kinetics for 3% crosslinked system.

$$V_r = V_r/(V_r + V_s) \tag{14}$$

where

$$V_r = m_1 d_s/[m_1(d_s - d_r) + m_2 d_r] \tag{15}$$

where m_1 is the weight of the polymer before swelling, m_2 is the weight of the polymer after swelling, d_s is the density of solvent, and d_r is that of the polymer. The polymer–solvent interaction parameter (χ) was determined from the Bristow and Watson semi-empirical equation (16):

$$\chi = \beta_1 + (V_s/RT)(\delta_s - \delta_p) \tag{16}$$

where β_1 is the lattice constant, usually about 0.34, V_s is the molar volume of solvent, R is the universal gas constant, T is the absolute temperature, δ is the solubility parameter, and the subscripts s and p refer to the solvent and polymer, respectively.

The molar volume of solvent is determined from the following equation:

$$V_s = M/d \tag{17}$$

where M is the molecular weight of solvent, and d is the density of solvent.

Crosslink density (CD) was calculated using eq. (18)[37]:

$$\text{CD}\ (\text{mol cm}^{-3}) = 1/(1.08 \times M_c) \tag{18}$$

where 1.08 is the density of polymer (in g cm^{-3}), and M_c is the number average molecular weight between crosslinks.

The above equations were used to compute the crosslink density. Toluene was chosen as it has a solubility parameter close to that of the base polymer, i.e., polybutyl acrylate. The behavior of triazole nodes toward toluene was not known. Its concentration in the polymer is limited to less than 3 mol % and it is not expected to impact the solubility characteristics of the polymer significantly expect serving as a crosslink point. In fact, it has been reported that when polypropylene oxide ($\delta = 18.6$ $MPa^{1/2}$) is transformed to its glycidyl azide polymer[40] and crosslinked via triazole, the solubility parameter increases to 22.4 $MPa^{1/2}$ (i.e., solubility parameter of the triazole network derived from glycidyl azide polymer[40] is 22.4 $MPa^{1/2}$ *vis-à-vis* a δ of 18.6 $MPa^{1/2}$ for polypropylene oxide). A comparison of the solubility parameter of polypropylene oxide[41] and triazole crosslinked polypropylene oxide (i.e., glycidyl azide–triazole) polymer, provided the group contribution of triazole group as $\delta = 26.3$ $MPa^{1/2}$. Every triazole in polybutyl acrylate is associated with a hydroxypropyl group. The latter's group contribution is $\delta = 25.5$ $MPa^{1/2}$, and the polybutyl acrylate has a $\delta = 18.4$ $MPa^{1/2}$. Solubility parameter of the triazole containing polybutyl acrylate was computed by the group contribution method based on these data, taking into account the unreacted and reacted azide groups (total 10 mol %).

Table III. Mc and Crosslink Density (CD) by Different Methods

	M_c (g mol^{-1})	CD (mol cm^{-3})	M_c (g mol^{-1})	CD (mol cm^{-3})	M_c (g mol^{-1})	CD (mol cm^{-3})
Crosslinker conc:	Expt.	Expt.	Theor.	Theor.	DMA	DMA
3	61,000	1.5×10^{-5}	42,700	2.2×10^{-5}	-	-
5	31,000	3.0×10^{-5}	24,650	3.8×10^{-5}	-	-
10	8200	11.0×10^{-5}	11,700	7.9×10^{-5}	12,900	7.1×10^{-5}

The solubility parameter of polybutyl acrylate-co-azido hydroxypropyl methacrylate (90 : 10) was computed as $\delta = 20.07$ MPa$^{1/2}$. Azide and triazole groups were assumed to have same group contribution. These values were used to compute the interaction parameter as per eq. (16) and the M_c in turn, as per eq. (13).

Theoretical crosslink density (based on simple, ideal statistics) for various extents of crosslinking and the experimentally determined crosslink densities are compared in Table III. The theoretical crosslink density was assessed from a statistical approach. The azide groups through which the crosslinking occurs were presumed to be distributed statistically in the polybutyl acrylate chain. For a copolymer with 10 mol % of azide groups, azide group was assumed to be located after every nine molecule of BuA. Incidentally, the propargyl groups are also located in the polybutyl acrylate at intervals of nine units of BuA. M_c was calculated as molar mass of segments between two azide groups, plus molar mass of five units of polybutyl acrylate–propargyl acrylate. For example, when the azide to propargyl ratio is 100 : 10, it is presumed that one out of every 10 azide groups serves as crosslinking sites; the distance between the crosslinks amounts to 100 units of monomers in poly(BuA-co-azidopropyl methacrylate). All the propargyl groups take part in the crosslinking. Thus, the contribution of propargyl acrylate is the same in all cases, i.e., 10 monomer units. A good match between the two confirms a normal crosslinking reaction between the two polymers.

As crosslinking diminishes, swelling index and rate of swelling increase. Swelling behavior is commensurate with crosslink density as per Flory–Rehner model and matches with the statistical calculation. Swell kinetics followed first order.

The crosslink density was estimated by dynamic mechanical thermal analysis (DMA) method for cross-verification in a typical case. The M_c and storage modulus are related by eq. (19):

$$M_c = 3dRT/E' \tag{19}$$

where E' is the Young's storage modulus, d is the density of the polymer, R is the universal gas constant, and T is the thermodynamic temperature which is $T_g + 40$ in K. For a typical polymer, a glass transition temperature of -20°C was obtained from DMA thermogram. From eq. (19), M_c was calculated as 12,900. A reasonably good match between the two validates the swelling method for estimating the extent of crosslinking.

CONCLUSION

Acrylic polymers bearing pendant propargyl and azide groups were synthesized by conventional free radical polymerization and chemical transformation. Propargyl groups were derived from the acid and azide groups from the epoxy-functional precursor polymer. The polymers could be effectively crosslinked through "click" reaction through the 1,3-dipolar cycloaddition reaction (Huisgen reaction) to form triazole network polymer. The crosslinking reaction followed a second-order kinetics, and the activation energy decreased with catalyst concentration. Copper(I) was found also to catalyze the decomposition of azide groups. The cure reaction is more sensitive to catalysis than the decomposition reaction of azide. The Huisgen reaction between the two groups led to a near-statistical crosslinking as assessed from the crosslinking density and swelling kinetics. The solvent swelling conformed to first-order kinetics, and the solvent diffusion was found to evolve from non-Fickian to Fickian model as crosslinking increased. The click reaction offered an alternate means to crosslink acrylate polymers.

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