Tailoring of energetic groups in acroyloyl polymers

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ABSTRACT
Acryloyl based novel energetic monomers having nitro acrylates and nitro triazole acrylates were synthesized and further used for polymerization. Due to scavanging properties of nitro groups, syntheses of nitro aromatic polymers are not facile at normal conditions. In this regard, we report a simple protocol to synthesize these energetic group embeded acroloyl polymers. These polymers were characterized by FTIR, and NMR spectroscopic techniques. gel permeation chromatography (GPC) technique was employed in order to understand molecular mass of these polymers along with average molecular weight, number average weight and poly dispersity index. Glass transition temperature ($T_g$) was determined by using DSC analysis. It was observed that with increase in nitro groups in polymers there is a decrease in glass transition temperature. Two steps degradation were depicted in the TGA thermograph in nitro containing polymers. Heat release during this reaction was found up to 951 J/g. Increase in nitrogen content in polymer unit enhanced the heat release of polymers.

1. Introduction
Acrylate polymers have ubiquitous applications in areas such as leather,[1] textile,[2] pharmacological drugs,[3] fiber optics,[4] metal complexes, polymer supports and building materials.[5] Studies of homopolymers, copolymers and blends acrylate have been reported in literature.[6] Introduction of phenyl ring into acrylate polymers, enhances the thermal stability which is useful in industrial applications such as peptide synthesis. Copolymer of Methyl methacrylates and phenyl acrylates exhibit photoluminscent properties.[7] Acrylamides are another class of acryloyl based polymers which are readily synthesized using primary amines.[8] Amine is an important functional group having multiple applications. Controlled radical polymerization of primary amines containing homopolymers and copolymers have been tolerant to many functional groups and variety of polar monomers.[9–11] Various types of controlled radical polymerization methods such as atom transfer radical polymerization (ATRP),[12] initiator-transfer-terminator polymerization,[13–15] nitroxide-mediated polymerization,[16,17] and reversible addition–fragmentation transfer polymerization (RAFT) [18] are reported in the literature. These acrylamide based polymers are useful in thermite application to bind the surface of nanoparticles.

However, energetic groups tailored aromatic acrylamide are not reported in the literature.

In addition to this another class of GAP based energetic polymers containing triazole and tetrazole ring are well known energetic materials.[20] Due to their sparing solubility in organic solvents, polymers containing tetrazoles as compared to triazoles are endeavored to a lesser extend in energetic applications. 1,2,3-triazole and 1,2,4-triazole compounds have directed recent attention as an energetic materials due to their high energy and nitrogen content. The heat of formation of 1,2,4-triazole and 1,2,3-triazole are 109 kJ/mol and 272 kJ/mol, respectively.[21]

Copper catalyzed 13-cycloaddition reaction is a powerful tool for the formation of triazole based polymers which involves the mechanism of Hüisingen cycloaddition.[22,23] Presently, few monomers have been synthesized in well-organized manner from organic azides and propargyl acrylate via copper catalyzed dipolar cyclo additions and further, polymerized using AIBN as a free radical initiator.

Energetic polymers are known to be useful in the field of nanoenergetic composites. Nanoenergetic materials are of great interest in combustion studies such as igniters and primers which are very useful for defence applications.[24] However, these materials are sensitive to impact, friction...
Instruments

\(^1\)H-NMR and \(^13\)C-NMR spectra were recorded on a Bruker-500 and 125 MHz instrument, respectively using tetramethylsilane (TMS) as an internal reference and DMSO-\(d_6\) as solvent. Coupling constants (J values) are given in Hertz (Hz). Chemical shifts are expressed in parts per million (ppm) downfield from internal reference, tetramethylsilane. The standard abbreviations s, d, t, q, quin, m and dd refer to singlet, doublet, triplet, quartet, quintet, multiplet and doublet of doublet respectively. IR spectra were recorded on a BRUKER ATR FT-IR spectrometer as a neat sample in the range of 500 to 4000 cm\(^{-1}\). High resolution mass spectra measurements were carried out on Micromass Q-Tof Mass spectrometer. Melting points were recorded on BUCHI M560. Differential Scanning Calorimetry (DSC) studies were carried out on a Perkin Elmer DSC-7 instrument operating at a heating rate of 10 °C/min in nitrogen atmosphere with 1 to 2 mg of sample. Thermal decomposition was also undertaken on a Perkin Elmer operating at a heating rate range from 10 °C/min.

2.3. General procedure for synthesis of N-(phenyl) acrylamide (1a–1e)

Substituted nitro aniline (36 mmol, 1 eq.) was dissolved in 100 ml of DCM in a two necked R.B. flask. Then the reaction mixture was kept for stirring 10–15 min under N\(^2\) atmosphere. Triethylamine (108 mmol, 3 eq.) was added dropwise at 0°–5 °C. Acroyl chloride (54.33 mmol, 1.5 eq.) was dissolved in 50 ml of dry DCM and was added dropwise with constant stirring. The reaction was continued for 1 h in cold condition and room temperature for 5 h. TLC was checked and the consumption of starting material was observed. Then the reaction mixture was diluted with the ethyl acetate (3 × 25 ml) and then washed with distilled water. Organic layer washed with brine solution and dried with anhydrous Na\(_2\)SO\(_4\). The organic layer was concentrated under reduced pressure. The crude product was purified by column chromatography by using ethyl acetate/ hexanes mixture as eluent.

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2. Experimental

2.1. Materials and methods

4-Nitroaniline (Sigma Aldrich), 3-Nitroaniline(Alfa Aesar), 3-(trifluoromethyl) aniline, 4-Nitro-2-(trifluoromethyl) aniline(Alfa Aesar), 3,5-dinitro aniline (Sigma Aldrich), 2,4-dinitro aniline (Sigma Aldrich), Sodium Azide (Sigma Aldrich), Copper Sulphate and Sodium ascorbate were used as received. Dichloromethane (Merck) was distilled. Triethyl amine was also distilled. Acryloyl chloride(Alfa Aesar) were used under inert conditions. AIBN (Sigma Aldrich) as obtained. All the solvents were purified by distillation prior to their use.

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2.3.2. N-(4-nitrophenyl) acrylamide (1b)
4.58 g, 65% yield, (20% EA+ n-Hexanes), m.p. 172 °C. 1H NMR (500 MHz, DMSO-d6) δ = 10.74 (br. s., 1 H), 8.24 (d, J = 8.5 Hz, 2 H), 7.91 (d, J = 9.2 Hz, 2 H), 6.56–6.25 (m, 2 H), 5.87 (d, J = 9.8 Hz, 1 H). 13C NMR (125 MHz, DMSO-d6) δ = 164.0, 145.7, 142.8, 131.7, 129.0, 125.5, 120.0. HRMS (Q-Tof) for C9H8N2O3 [M+H]+ calc. 215.0532 found 215.0535.

2.3.3. N-(3-(trifluoromethyl) phenyl) acrylamide (1c)
5.21 g, 78% yield, (23% EA+ n-Hexanes)m.p. 87 °C. 1H NMR (500 MHz, DMSO-d6) δ = 10.46 (s, 1 H), 8.19 (s, 1 H), 7.87 (d, J = 8.9 Hz, 1 H), 7.54 (t, J = 7.9 Hz, 1 H), 7.42–7.34 (d, J = 10 Hz, 1 H), 6.62–6.40 (m, 1 H), 5.79 (dd, J = 2.1, 10.1 Hz, 1 H). 13C NMR (125 MHz, DMSO-d6) δ = 164.0, 140.3, 131.9, 130.4, 130.3, 130.16, 130.03 (q, J = 31.25 Hz), 129.66, 127.9, 125.6, 122.4. 19F NMR (CDCl3, 376 MHz) δ = 253.3 Hz), 121.4, 119.2, 117.8. 19F NMR (CDCl3, 376 MHz) δ = –62.7 (3F, s, CF3). HRMS (Q-Tof) for C10H8F3NO [M+H]+ calc. 237.0386 found 237.0386.

2.3.4. N-(4-nitrophenyl)-3-(trifluoromethyl) phenyl acrylamide (1d)
5.16 g, 80% yield, (40% EA+ n-Hexanes)m.p. 153 °C. 1H NMR (500 MHz, DMSO-d6) δ = 10.88 (br. s., 1 H), 8.28 (s, 1 H), 8.19–8.01 (m, 2 H), 6.48–6.28 (m, 2 H), 5.86 (d, J = 9.8 Hz, 1 H). 13C NMR (125 MHz, DMSO-d6) δ = 164.5, 144.1, 141.8, 131.3, 129.3, 128.01, 125.7, 123.9, 124.6 (q, J = 33.7 Hz) 123.53, 123.46 (q, J = 33.7 Hz), 123.07, 122.73, 122.31 (q, J = 253.3 Hz), 121.4, 119.2, 117.8. 19F NMR (CDCl3, 376 MHz) δ = –60.0 (3F, s, CF3). HRMS (Q-Tof) for C12H9F3N2O3 [M+H]+ calc. 260.0432 found 260.0409.

2.3.5. N-(35-dinitro phenyl acrylamide) (1e)
1.71 g, 65% yield, (52% EA+ n-Hexane)m.p. 179 °C. 1H NMR (500 MHz, DMSO-d6) δ = 11.04 (s, 1 H), 8.92 (d, J = 2.1 Hz, 2 H), 8.52 (d, J = 2.1 Hz, 1 H), 6.53–6.24 (m, 2 H), 6.05–5.75 (m, 1 H). 13C NMR (125 MHz, DMSO-d6) δ = 164.7, 148.7, 141.5, 131.2, 129.7, 119.1, 113.0. HRMS (Q-Tof) for C13H7F3N2O3 [M+H]+ calc. 237.0386 found 237.0386.

2.4. General procedure for synthesis of 1(1-phenyl)-1H-1,2,3-triazol-4-yl acrylate (2a–2c)
1-azido-3-nitrobenzene (5.44 mmol, 1 eq.) was taken in 30% t-butanol-water mixture. In this reaction mixture of prop-2-yn-1-yl acrylate (6.53 mmol, 1.2 eq.) and copper sulphate (1.08 mmol, 0.2 eq.), and sodium ascorbate (0.54 mmol, 0.1 eq.) were added. Then the reaction mixture was stirring at room temperature for overnight. TLC was analyzed and it showed consumption of starting material. The reaction mixture was diluted with ethyl acetate (3 × 25 ml) and washed with distilled water, brine solution and dried using anhydrous Na2SO4. The organic layer was concentrate under reduced pressure. The crude products were purified by column chromatography by using ethyl acetate/hexanes mixture as the eluent.

2.4.1. (1-(3-nitrophenyl)-1H-1,2,3-triazol-4-yl) acrylate (2a)
1.72 g, 68% yield, (57% EA+ n-Hexanes) m.p. 88 °C. 1H NMR (500 MHz, CHLOROFORM-d) δ = 8.63 (t, J = 2.1 Hz, 1 H), 8.33 (ddd, J = 0.9, 2.1, 8.2 Hz, 1 H), 8.24 (s, 1 H), 8.20 (ddd, J = 0.9, 2.1, 8.2 Hz, 1 H), 7.78 (t, J = 8.2 Hz, 1 H), 6.49 (dd, J = 1.4, 17.2 Hz, 1 H), 6.18 (ddd, J = 10.4, 17.4 Hz, 1 H), 5.91 (dd, J = 1.410.5 Hz, 1 H), 5.43 (s, 2H).

2.4.2. (1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl) acrylate (2b)
1.77 g, 71% yield, (55% EA+ n-Hexanes) m.p. 110 °C. 1H NMR (500 MHz, CHLOROFORM-d) δ = 8.48–8.42 (m, 2 H), 8.22 (s, 1 H), 8.04–7.96 (m, 2 H), 6.47 (dd, J = 5 Hz, 1 H), 6.23–6.13 (m, 1 H), 5.92 (d, J = 10 Hz, 1 H), 5.43 (s, 2 H).

2.4.3. (1-(3-trifluoromethyl phenyl)-1H-1,2,3-triazol-4-yl) acrylate (2c)
1.35 g, 66% yield, (51% EA+ n-Hexanes) m.p. 110 °C. 1H NMR (500 MHz, CHLOROFORM-d) δ = 8.18 (s, 1 H), 8.03 (s, 1 H), 7.97 (d, J = 5.0 Hz, 1 H), 7.76–7.65 (m, 2 H), 6.46 (dd, J = 1.4, 17.2 Hz, 1 H), 6.16 (dd, J = 10.4, 17.4 Hz, 1 H), 5.89 (dd, J = 1.4, 10.5 Hz, 1 H), 5.41 (s, 2 H).

2.5. General procedure for polymerization (3a–3h)
(5.25 mmol, 1 eq.) of N-(phenyl) acrylamide and (0.105 mmol, 0.2 eq.) of AIBN were dissolved in 1,4-dioxane, flushed with nitrogen gas for 20 min and then reaction mixture was heated to 100 °C and reaction continued for 24 h under inert atmosphere. The color of the solution changed from grey to brown. During monitoring of reaction mixture by TLC, it was observed that starting material was consumed and a new spot was noticed at the bottom.
of the TLC. Methanol was slowly added to the reaction mixture to precipitate the polymer. The precipitate was further washed 2–3 times with methanol and then dried in oven at 50 °C.

### 2.5.1. Poly (N-(3-nitrophenyl) acrylamide) (3a)

0.310 g, 62% yield. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta = 10.63–9.96\) (m, 1 H), 8.35–7.49 (m, 2 H), 5.84–4.92 (m, 2 H), 2.61–2.20 (m, 1 H), 1.87–1.31 (m, 1 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 172.7, 140.4, 132.1, 130.5, 123.5, 119.91, 116.06, 29.51, 21.6.

### 2.5.2. Poly (N-(4-nitrophenyl) acrylamide) (3b)

0.321 g, 64% yield. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta = 10.77–10.10\) (m, 1 H), 8.27–7.32 (m, 3 H), 2.51 (d, \(J = 1.7\) Hz, 1 H), 2.12–1.53 (m, 1 H), 1.38–0.76 (m, 1 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 173.7, 147.9, 140.6, 129.9, 125.8, 117.7, 113.9, 35.9, 26.9.

### 2.5.3. Poly (N-(3-(trifluoromethyl) phenyl) acrylamide) (3c)

0.354 g, 75% yield. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta = 10.16–9.71\) (m, 1 H), 8.14–7.43 (m, 2 H), 7.36–7.02 (m, 1 H), 2.61–2.17 (m, 1 H), 2.06–1.55 (m, 1 H), 1.45–1.13 (m, 1 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 173.6, 140.2, 129.5, 123.5, 123.09, 120.4, 119.6, 116.3, 35.4, 26.9.

### 2.5.4. Poly(N-(4-nitrophenyl)-3-(trifluoromethyl) phenyl) acrylamide) (3d)

0.278 g, 58% yield. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta = 10.84–10.33\) (m, 1 H), 8.35–7.49 (m, 2 H), 2.61–2.20 (m, 1 H), 2.04–1.35 (m, 2 H), 1.29–0.90 (m, 1 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 178.8, 148.8, 146.2, 132.3, 128.1, 127.4, 125.9, 123.8, 122.5, 41.1, 29.1.

### 2.5.5. Poly (N-(35-dinitro phenyl acrylamide) (3e)

0.256 g, 51% yield. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta = 11.17–10.65\) (m, 1 H), 9.18–8.08 (m, 2 H), 2.23–1.90 (m, 1 H), 1.87–0.90 (m, 3 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 172.7, 140.4, 132.1, 130.5, 123.5, 119.91, 116.06, 29.51, 21.6.

### 2.5.6. Poly (1-(3-nitrophenyl)-1H-123-triazol-4-yl) acrylate (3f)

0.362 g, 62% yield. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta = 9.14–8.62\) (m, 1 H), 8.57–7.50 (m, 3 H), 5.45–4.79 (m, 2 H), 2.43–2.06 (m, 1 H), 1.92–1.42 (m, 2 H), 1.34–0.97 (m, 1 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 171.4, 148.6, 143.6, 137.2, 131.8, 126.1, 123.4, 114.9, 57.635.025.8.

### 2.5.7. Poly (1-(4-nitrophenyl)-1H-123-triazol-4-yl) acrylate (3g)

0.367 g, 63% yield. \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta = 9.08–8.62\) (m, 1 H), 8.44–7.85 (m, 2 H), 5.44–4.96 (m, 1 H), 2.60–2.23 (m, 1 H), 2.07–1.56 (m, 1 H), 1.45–0.99 (m, 1 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 174.2, 147.02, 143.78, 140.83, 125.83, 123.3, 120.9, 57.8, 34.3, 25.9.

### 2.5.8. Poly (1-(3-trifloromethyl phenyl)-1H-123-triazol-4-yl) acrylate (3h)

0.421 g, 80% yield, \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta = 9.13–8.56\) (m, 1 H), 8.36–7.92 (m, 2 H), 7.88–7.50 (m, 2 H), 5.38–4.92 (m, 2 H), 2.48–2.11 (m, 1 H), 1.94–1.50 (m, 2 H), 1.37–0.95 (m, 2 H). \(^13\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta = 174.1, 143.4, 137.3, 131.6, 127.2, 125.6, 124.2, 123.6, 122.8, 120.6, 117.1, 57.6, 35.2, 26.6.

### 3. Results and discussion

Attempt was made in this study to synthesize acrylate monomers having various substituents. Initially, various reaction parameters were examined using different kinds of reaction conditions for synthesis of acrylate monomers (Table 1). For the reaction between aromatic amine and acryloyl chloride, we attempted reaction with triethyl amine as a base and DCM as solvent to get the product as substituted acrylamide (Scheme 1). By using the above mentioned optimized method, five aromatic substituted acrylamide were synthesized. The substitution was done with energetic groups such as –NO\(_2\), and –CF\(_3\). The structure of the aromatic acrylamide monomers was characterized. Yield of the nitro containing polymers are observed to be very less due to their electron withdrawing nature. In–CF\(_3\) molecule when –H is replaced by fluorine, density of the hydrocarbon will be increased. While –CF\(_3\) possessing monomers yield is high. Finally, the desired products of monomers were obtained after optimizing the conditions with good amount of yield. The structure and the yield of various monomers are described below in Table 2.

### Table 1. Different conditions to optimized the reaction.

| Compound | Reaction mixture | Temperature (°C) | Time (h) | Yield (%) |
|----------|-----------------|-----------------|----------|-----------|
| 1(b) Triethylamine/ethyl methyl ketone 0 for 1 h and 25 for 5 h | 6 | 57 |
| K\(_2\)CO\(_3\)/acetone 0 for 1 h | 6 | 55 |
| Triethylamine/dichloromethane 0 for 1 h and 25 for 5 h | 6 | 65 |

![Scheme 1. Synthesis of N–phenyl acrylamide.](image-url)
After synthesizing energetic group embedded acrylamide monomers, we ventured upon to synthesize triazole based acrylate esters. The formation of the acrylic monomers (2a–2c) was accomplished by using copper-catalyzed 13-dipolar cycloaddition of the organic azides [26] with propargyl acrylate. The reaction was carried out under mild conditions for 8–10 h at room temperature in water and t-butanol mixture (Scheme 2) and structure of different triazole acrylate monomers are mentioned in Table 3.

### 3.1. Polymerization

After accomplishing acrylamide (1a–1e) and acrylate monomers (2a–2c), we attempted radical polymerization reaction by various methods. In polymerization step, different conditions were endeavoured (Table 4), but the yield of the desired polymer was low. After several efforts, changing the solvent to dioxane & AIBN as radical initiator, better yields were obtained as listed in Table 5. After 12 h the color of the reaction mixture turned brown & then product formed were precipitated in the methanol. The yield of the polymerization ranged from good to better. The good yield of the –CF₃ possessing polymer was observed as mentioned above. Reactions of the acrylamide and acrylate polymers are shown in Schemes 3 and 4.

The triazole based polymers (3f–3h) were synthesized by the same procedure and the yields of the polymers are mentioned in Table 6.
the yield obtained was not equivalent with that of conventional heating method as described above and also scaling up of this reaction was difficult. Hence we concluded that conventional heating gave better yield of poly nitro acrylamide as compared to microwave heating.

Attempts to do polymerization at lower temperature (less than 70 °C) showed lower yield because fewer radicals were generated at low temperature leading to incomplete conversion to polymer. Generally, polymerization step is reported to be carried out at 70 °C, but in our case presence of nitro and di nitro polymerization took place at relatively higher temperature ~100 °C. Increasing the number of nitro group in aromatic ring retards the reactivity of monomer. In 35 dinitro acrylamide (3e) presence of two nitro groups lowers the yield of the polymer. On the other hand, 246 trinitro acrylamide did not show polymerization reaction due to the presence of three nitro groups which act as scavenger to free radicals thereby inhibiting the polymerization reaction.[27]

The structure of compounds (3a–3h) was confirmed by different techniques. FTIR spectra of compound (1a–1e) exhibit the presence of peaks in the range cm$^{-1}$, 1665–1690 (–CONH), 1493–1595(Aromatic –C=C–), 1327 & 1520(–NO2), ~1240 (–C=C). During polymerization a new peak was generated at ~2940 cm$^{-1}$, which confirms that the double bond peaks has been reduced to as happening during the polymerization step was successfully done. (Supporting Information) In similar way, 1H NMR spectra of polymer (3a–3h) ~6.50–6.25(s, 1H) and ~5.8(s, 1H) peaks disappeared and a new peak ~1.26–2.55(–CH2) was observed, this peak indicates that –CH=CH2 changes into methylene group. In carbon NMR, two additional new peaks were observed around 25 and 37 ppm and corresponding to saturated carbon atoms. (Figure 1). In Figure 2,

![Scheme 5. Synthesis of poly (3 nitro-phenyl) acrylamide 3(a).](image)

![Figure 1. 1H NMR of monomer 1(a) & polymer 3(a).](image)
3.2. Molecular weight

Molecular weight of polymers was determined by GPC. Number and weight average molecular weight, polydispersity index were determined and are represented in Table 7. The average polydispersity indexes of the polymers are in the range of 1.00 to 1.74. Molecular weights of nitro based polymers (3a–3h) (2700–9000) are in good agreement with the reports present in the literature.[28] Nitro group acts as a radical scavenger and hence the presence of nitro groups in polymer backbone retards the growth

Figure 2. $^{13}$C NMR of monomer 1(a) & polymer 3(a).
of polymer chain. Further, the decrease in polymer weight in 3(c) and 3(d) was observed. The presence of bulky and electron withdrawing group (–CF₃) in both the monomers prevents attaining high molecular weight, which may be due to reduced approach of monomers and also the electron withdrawing effect weakening –NH bond for favored chain transfer to monomer. In the case of polymer (3 h) even in presence of –CF₃ group, the molecular weight is enhanced. The presence of –CF₃ group being far away from the double bond may not interfere by reducing the reactivity. Further, the hydrogen bonding increases the viscosity. Under this condition, the rate of termination of polymer radicals becomes diffusion controlled. As highly viscous medium is present the termination rate becomes very low making the overall rate of increase of polymerization

Table 7. Molecular weight of polymers.

| Polymer | $M_w$ Average | $M_n$ Average | PDI $M_w/M_n$ |
|---------|--------------|--------------|---------------|
| 3(a)    | 5448         | 4097         | 1.33          |
| 3(b)    | 8314         | 8314         | 1.00          |
| 3(c)    | 2791         | 2791         | 1.00          |
| 3(d)    | 2791         | 2791         | 1.00          |
| 3(f)    | 8985         | 5146         | 1.74          |
| 3(g)    | 3877         | 2216         | 1.74          |
| 3(h)    | 48,938       | 31,798       | 1.53          |
higher (Equation 1). Further, the monomer being a small molecule, the mobility is not much affected and molecular weight continues to increase. Moreover it reduces the rate of termination of polymer radicals which also leads to increase of molecular weight. The rate of polymerization \( R_p \) is expressed as:

\[
R_p = k_p[M]\left(\frac{f k_d}{k_t}\right)^{\frac{1}{2}}
\]  

(1)

Where \( M \) is the monomer, \( f \) is the mole fraction of free radical initiator which initiate the polymerization, \( I \) is the initiator, \( k_p, k_d, \) and \( k_t \) are the constants for chain propagation, initiator dissociation, and termination.

### 3.3. Thermal studies

The thermograms of all the synthesized polymers except poly 3NA (3a), poly 3TrZ(3f) and poly 4TrZ (3 g) clearly indicates that they undergo single stage decomposition. The two stage decomposition of poly 3NA, poly 3TrZ and poly 4TrZ can be explained (Figures 5 and 6) by taking into consideration the following mechanism. The first step of decomposition implicates the loss of CO\(_2\), breaking of

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**Figure 4.** \(^{13}\)C NMR of triazole monomer 2(a) & polymer 3(f).
observed suppression of \( T_g \) values is due to presence of electron withdrawing groups (\(-\text{NO}_2, -\text{CF}_3\)) in the polymer backbone.[18]

### 3.4. Oxygen balance (O.B.)

Oxygen balance is an important parameter to explain the sensitivity and degree of explosion, where an explosive material can be oxidized. Oxygen balance (O.B.) is expressed as,

\[
\text{O.B.}(\Omega)\% = \frac{-1600}{\text{Molecular weight of compound} \left( \frac{2X + Y}{2} + M - Z \right)}
\]

Where \( X \) = number of atoms of carbon, \( Y \) = number of atoms of hydrogen, \( Z \) = number of atoms of oxygen and \( M \) = number of atoms of metal (if metallic oxide produced).

Mostly energetic molecules possess negative oxygen balance, it means these materials require oxygen to combust. Oxygen is needed to convert all C into CO\(_2\) and H into H\(_2\)O. O.B. of the polymers which we have described in the present work lies in the range of \(-111.37\) to \(-174.95\)\% (Table 9) which is almost similar to energetic binders which are used in propellant formulations such as GAP\((-121\%)\), Poly-BAMO\((-124\%)\), Poly-AMMO\((-170\%)\), and Poly-NIMMO\((-114\%)\).[30] But polymers which we are describing here possess explosphores groups such as nitro and triazole, hence these types of polymers are comparable to other energetic materials.
4. Conclusions

Herein, we report the synthesis of novel energetic acrylamide/acylate polymers which consist of energetic groups like –NO$_2$,–CF$_3$ and nitropheryl substituted triazole. Generally, the synthesis of these polymers may be difficult under normal conditions because of electron withdrawing nature. We have adopted a simple methodology to synthesize these molecules. These molecules demonstrate high heat release and better thermal stability. In addition, low value of glass transition temperature and increase in enthalpy of formation were found due to the increase of nitrogen content in polymer backbone. Molecular weights of the polymers were reduced due to the nitro group present in polymer network. Nitro group behaved like a scavenger in free radical polymerization. Nitro group containing polymers decomposed in two steps whereas others are found to be single step decomposition. All these properties of the nitro and trifluoro containing polymers make them a good candidates for energetic applications.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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