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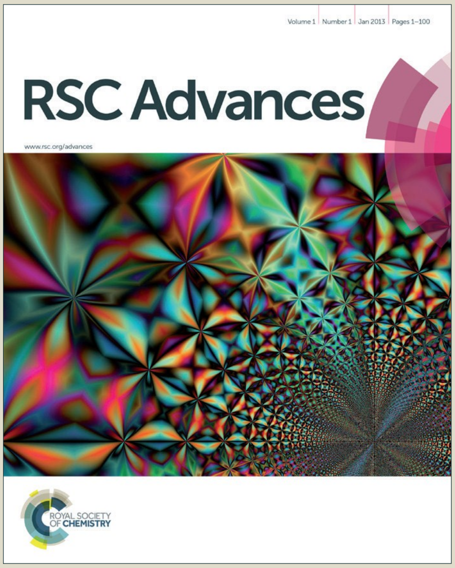

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Synthesis of Bis(propargyl) Aromatic Esters and Ethers: A Potential Replacement for Isocyanate Based Curators

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Abstract

This paper reports the synthesis and characterization of novel class of non-isocyanate curing agents based on bis-propargyl aromatic esters **2a-e** and ethers **4a-c**. Total eight non-isocyanate curators have been prepared from the reaction of respective dicarboxy- or dihydroxybenzene with propargyl bromide in presence of potassium carbonate with good yields. The structure and purity of synthesized compounds and the corresponding intermediates were confirmed by spectral (IR & NMR), thermal (DSC) and chromatographic techniques (HPLC & GC-MS). Further, kinetics of curing reaction between Glycidyl azide polymer (GAP) and synthesized alkynes (**4b, 4c**) were studied by using FT-IR spectroscopy as a function of time at different temperatures viz. 303, 323, 333 K. It was found that curing reaction is faster while increasing the temperature. Kinetic parameters of curing reaction such as order of reaction and activation energy were calculated for the GAP-4a and GAP-4c systems. All the curing reaction follows first order and corresponding activation energy of curing reaction for the systems were found to be 15.56, 13.22 kcals/mol respectively. For comparison, curing studies were performed for GAP with conventional curator Desmodur N-100. GAP cured with non-isocyanate curators offers good mechanical properties as compared to GAP cured with isocyante (N-100). The advantage of these new curing systems does not require catalyst and no need of specific environmental conditions. Based on this studies, 1,4-Bis(2-propynyloxy)benzene (**4b**) is the most potential non-isocyanate curator for azide polymeric binders.

Keywords: Non-isocyanate curators; Characterization; Azidopolymers; Curing kinetics; Propellants

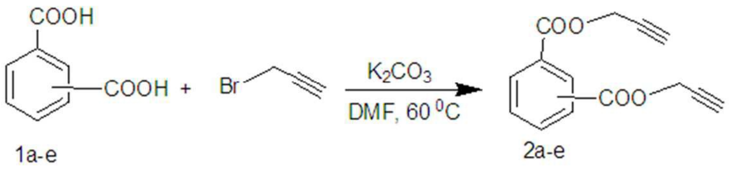
1 Introduction

There is constant effort for the development of high performance composite propellant formulations to meet the future requirement. The performance of composite propellant formulations can be enhanced by the addition of energetic oxidizers like ammonium dinitramide (ADN), hydrazinium nitroformate (HNF) as well as an energetic binder like GAP. GAP is usually cured by the reaction with polyisocyanates to form polyurethane network. However, isocyanates are hazardous and moisture sensitive. They react with moisture to release CO_2 and form voids in the cured propellant, leading to poor mechanical properties. For these reasons, use of non-isocyanate curing agents are of great interest.[1-3] Particularly for ammonium dinitramide (ADN), such non-isocyanate curing agents would be very useful due to the severe compatibility issues between ADN and isocyanates. Hence, an alternate approach perceived to exploit the 1,3-dipolar cycloaddition reaction between azide group of GAP and triple bond of alkynes (Huisgen reaction) forming 1,2,3-triazoles. This is a versatile tool in polymer chemistry for realizing cross-linked networks without any side reaction and thus is a prime example of Click chemistry.[4-6]

Poly-functional alkynes are potential isocyanate free curing agents for hydroxyl functional azido polymers which are cured by thermal, non-catalyst reaction with alkyne to form triazole cross-linked energetic binders. Azido polymers can be cross-linked through some or all of the azido groups with multifunctional dipolarophiles having reactive groups selected from acrylic and acetylenic esters or amides to produce a polymer material comprising triazoline or triazole groups. Triazole formation is favored by electron donating groups on the azide whereas electron withdrawing groups on the alkynes.[7,8] The presence of electron withdrawing groups at the vicinity of alkynes is much preferred due to its better reactivity towards cycloaddition reaction at ambient temperature. In addition to this, introduction of nitro groups in the acetylenic moiety adds more energy to the propellant systems. The presence of triazole groups in the cross-linked polymer is expected to enhance the thermal stability and burn rate.[9] Earlier studies have reported[10,11] that the curing of GAP with an alkynes such as bis-propargylsuccinate(BPS), 1,4-Bis(1-hydroxypropargyl)benzene(BHPB) and bisphenol-bis(propargyl ether) (BABE) to form triazole network with azide polymers. ADN/GAP propellant cured with BPS was investigated and found that burning rate was slightly higher than isocyanate cured propellants.[3] Potinus Heike[12] et al studied heat generation rates of GAP with either isocyanate or BPS by heat flow microcalorimetry and their compatibility with ADN. This paper reports the synthesis of alkynes based bis-propargyl aromatic esters **2a-e** and ethers **4a-c** with the aim of alternative to existing isocyanate curing agents for energetic azido polymers. Further, we have also reported kinetics of curing reaction between GAP and selected curators (**4b, 4c**) and compared with GAP cured with Desmodur N-100 using quantitative FTIR spectroscopy.

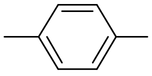
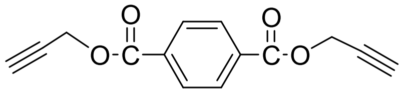
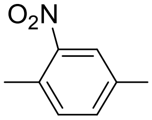
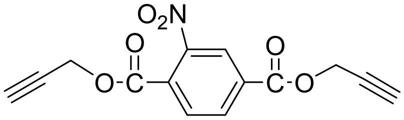
2 Results and Discussion

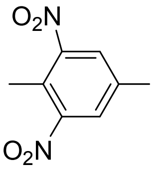
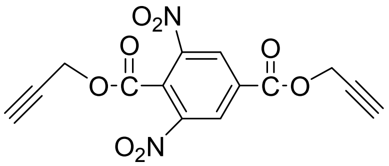
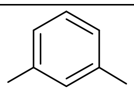
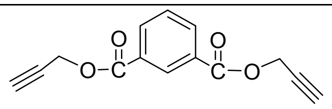
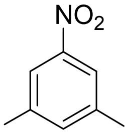
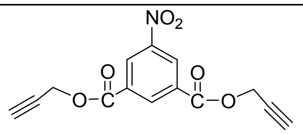
Synthesis of compounds 2a-e and 4a-c



Scheme 1. Synthesis of bis-propargyl-aromatic esters (**2a-e**)

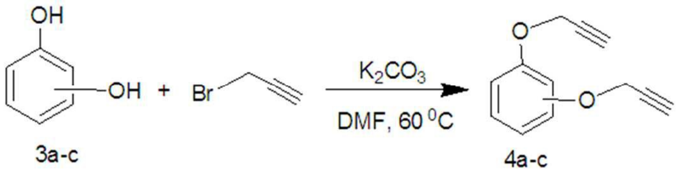
Table 1. Structures and yield of compounds **2a-e**

Entry	-Ar-	Product	m.p. ($^{\circ}$C)*	Yield (%)$^{\#}$
1.	 **(1a)**	 **(2a)**	110.5	54
2.				

	(**1b**)	(**2b**)	88.38	61
3.	 (**1c**)	 (**2c**)	89.98	62
4.	 (**1d**)	 (**2d**)	85.53	85
5.	 (**1e**)	 (**2e**)	145.54	70

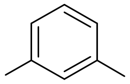
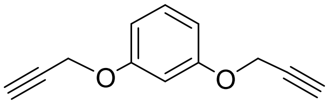
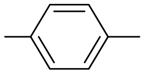
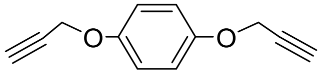
* m.p. determined using DSC technique.

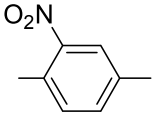
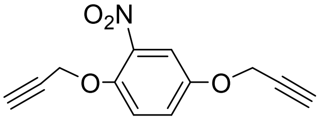
\# Yields are based on column purification



Scheme 2. Synthesis of bis-propargyl-aromatic ethers (4**a-c**)

Table-2. Structures and yield of compounds 4a-c

Entry	-Ar-	Product	m. p.(°C)*	Yield (%)#
1	 **(3a)**	 **(4a)**	40.69	47
2			48.92	56

	(3b)	**(4b)**		
3	 **(3c)**	 **(4c)**	76.31	46

* m.p. determined using DSC technique, $^{\#}$ Yields are based on column purification

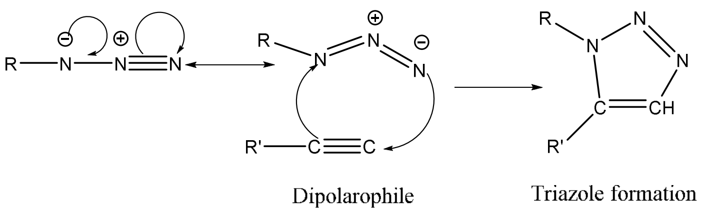
The work presented herein involves synthesis and characterization of bis-propargyl aromatic esters **2a-e** and ethers **4a-c** which are potential non-isocyanate curators for energetic azido binders for development in advanced smokeless composite rocket propellant system. The compounds **2a-e** and **4a-c** were synthesized by reacting corresponding dicarboxy or dihydroxybenzene with propargyl bromide under mild reaction conditions. The products **2b**, **2c** and **2e** were synthesized for the first time and characterized (**Scheme-1**). The compounds **2a** and **2d** were synthesized by modifying the literature methods.[13,14] The reported methods involve the use of expensive 4-(dimethylamino)pyridine(DMAP) as base following a tedious workup process. Our method used K_2CO_3 as base and a simple workup process gave good yields (**Table-1& 2**). The compound **4c** was synthesized (**Scheme-2**) for the first the time along with compounds **4a**, **4b** based on reported methods.[15,16] The synthesis route and its structural characterization are presented in this paper. For comparison, intermediate compounds **1b, 1c, 1d** and **3c** were also synthesized based on literature procedures.[7,17-20]

Structural characterization

The structure of compounds **2a-e** and **4a-c** were confirmed by IR, NMR and mass spectroscopy. FTIR spectra of compounds **2a-e** show presence of $-\mathrm{C}\equiv\mathrm{C}-$ bond with absorption in the range 2127-2133 cm^{-1}, while alkyne proton (-C≡C-H) stretching absorption are in the range 3269-3294 cm^{-1}. The ketonic >C=O group of synthesized nitro dicarboxylic acids (intermediates) are at 1705 cm^{-1} while the >C=O group of esters exhibited stretching absorption in the frequency range 1716-1785 cm^{-1}. FTIR results of bis-propargyl aromatic ethers **4a-c** showed characteristic absorption peak of -C≡CH stretching between 3282-3289 cm^{-1}, $-\mathrm{C} \equiv \mathrm{C}-$ bond absorption peak at 2127-2133 cm^{-1} and C-O-C absorption peak between1030-1091cm^{-1}. Compounds **2b**, **2c**, **2e** & **4c** showed peaks at 1546 and 1328 cm^{-1} corresponding to NO_2 stretching frequencies. All protons were observed in the ^{1}H-NMR spectra of compounds **2a-e** and **4a-c** with the expected chemical shifts and integral values. The ^{13}C-NMR spectra of compounds **2a-e** and **4a-c** showed the number of signals which were consistent with the number of carbon atoms in the molecule (Supporting information). The products **2a-e** and **4a-c** were subjected to GC-MS analysis. The results obtained from gas chromatograph showed single peak and corresponding mass spectra of compounds **2a-e** & **4a-c** showed molecular ion peak M^{+} at m/z in agreement with their molecular formula. Purity of compounds **2a-e** and **4a-c** were determined by RP-HPLC and were found to be greater than 98 %.

Curing kinetics of GAP with bis-propargyl ethers

Triazole cross-linked networks are readily formed by the 1,3-dipolar (3+2) cycloaddition between azide group of GAP and triple bond of alkynes without catalyst. The possible mechanism of formation of triazole ring is shown in **Scheme-3**. The required reaction time for formation of triazole cross-linked networks was from 24 h to one week. This is due to the low reactivity of acetylenic compounds towards 1,3-dipolar cycloaddition reactions. The acetylene bond is deactivated by introducing electron withdrawing groups in the vicinity of the molecule.[8] Therefore, deactivating groups like nitro, carbonyl and aryl moiety are intentionally introduced to meet required curing conditions in the temperature range of 35-50°C.[21]



Scheme 3: Possible mechanism of curing reaction between GAP and an alkyne compound

GAP (molecular weight ~ 1800) and curator **4b** or **4c** (30% of GAP, w/w) were mixed at room temperature and degassed applying vacuum. Curing reaction was monitored by FTIR spectroscopy as a function of time at different temperatures (303, 323 & 333K). The curing reaction was monitored by observing the change in the intensity of the absorption band at 3285cm^{-1} corresponds to alkyne proton (-C≡CH) and found to be decrease as the curing reaction proceeded **(Figure 1).** Absorption peak at 2094 cm^{-1} indicates that presence of residual azido groups in the GAP. Characteristic peaks of triazole ring after curing was observed in the range 1500-1300 cm^{-1} corresponds to N=N & C=C bonds. Curing kinetics of triazole formation between GAP and curator was carried out by evaluating the change in the intensity of alkyne proton (-C≡CH) stretching band at 3285 cm^{-1}. Intensity of the absorption band for -C≡CH stretching was calculated by taking the integral of the band between 3310-3100 cm^{-1} by using OMNIC software.[22] The standard equation was used to analyze the curing profile of GAP-with curators **4b** or **4c**.[23,24] A plot of change in concentration of **4b** and **4c** as a function of time at different temperature is shown in the Figure 2 and 3. It indicates that at room temperature (303K) curing reaction required 18-30 hrs for gel formation. As the cure temperature increases curing time decreases to 3 hr. It was observed that the gelation occurs after conversion of 55-60% curing and this value can be served as semi-quantitative estimate of gel point. The required curing time for gel formation at different temperatures for the system GAP-4b and GAP-4c systems are summarized in the **Table-3** along with conventional curators for comparison. The results are indicated that gel time is faster for nitro substituted curator (**4c**) than that of without nitro group (**4b**). The rate of reaction of curator with and without electron deficient group (NO_2) was studied (Table 4). For example, curator having nitro group (**4c**) showed higher rate of reaction as compared curator without nitro group (**4b**). The rate constant at different temperatures is given by the Arrhenius equation, lnk = ln A-(E_a/RT). The activation energy (E_a) for the curing reaction was calculated from Arrhenius equation, by plotting ln(k) versus 1/T (**Figure- 5**). Measured activation energy for curing reaction of GAP-4b and GAP-4c systems are 15.56 and 13.22 kcal/mol respectively. It is further evidence that effect of nitro group present in the curators.

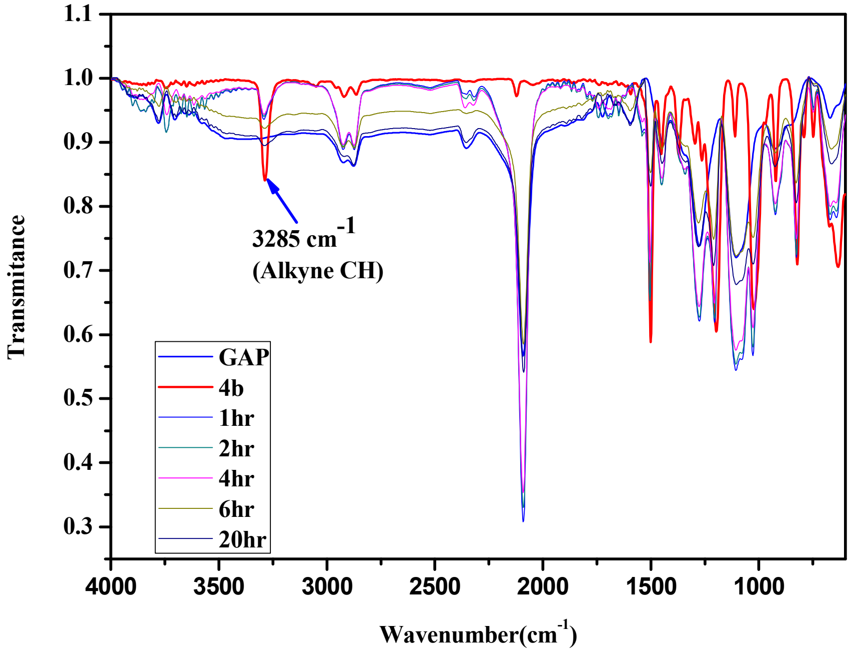


Figure 1 FTIR Spectrum of pure GAP and GAP cured with **4b** at different time interval.

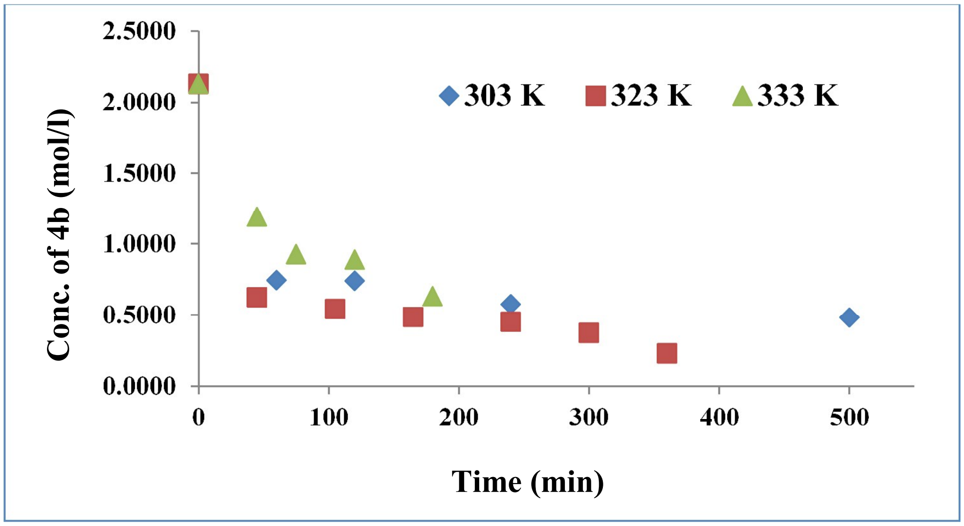


Figure 2 Change in concentration of **4b** during curing with GAP.

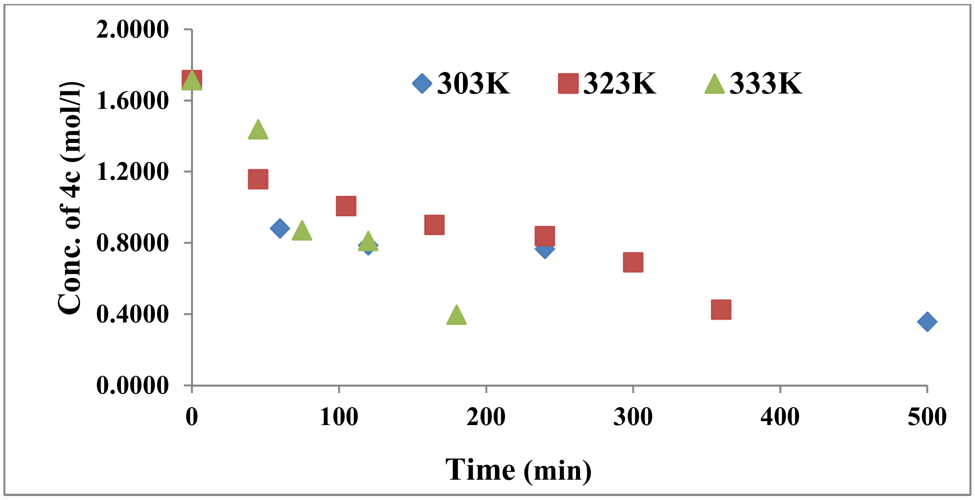


Figure 3 Change in concentration of **4c** during curing with GAP.

Table 3 Gel time profile for curing of GAP-N100 and GAP-**4b/4c.**

Temperature (K)	GAP + 4b	GAP + 4c	GAP+N-100+Catalyst
303	23 hr	25 hr	30hr
323	3.5 hr	3.0 hr	-
333	2.5 hr	2.3 hr	3.7 hr[25]

Table 4 The rate constants for the GAP-4b & GAP-4c systems.

Temperature(K)	GAP+4b system s^{-1}	GAP+4c system s^{-1}
303.15	0.0005	0.00047
323.15	0.0024	0.00138
333.15	0.0048	0.00375

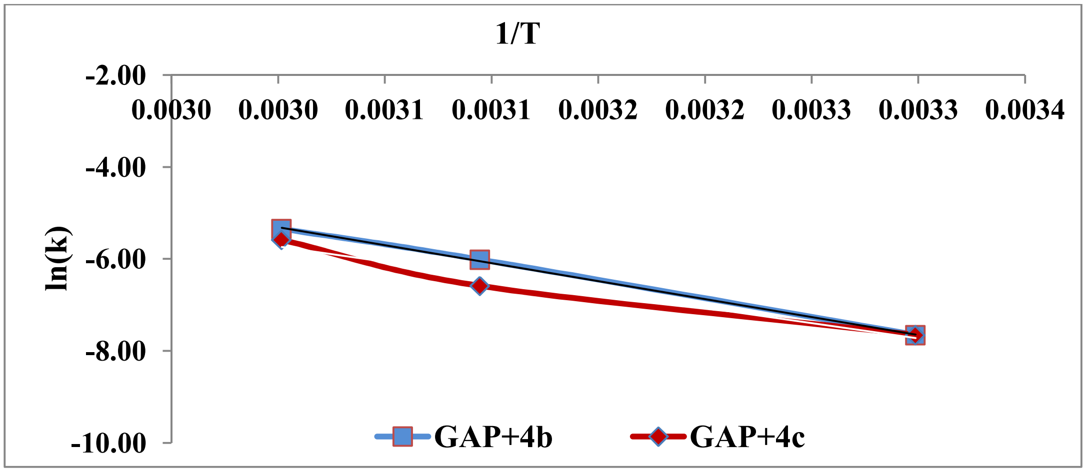
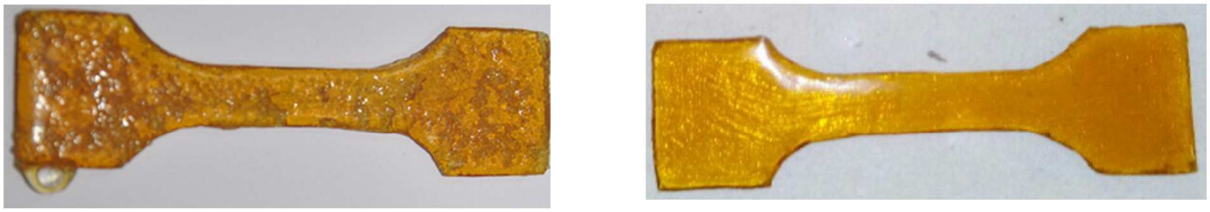


Figure 4 Plot of ln (k) verses 1/T for the two systems

Figure 5 show the GAP cured with isocyanate in presence of catalyst at room temperature without humidity control. Similarly GAP cured with non-isocyanate (**4b**) curator at same condition without catalyst for comparison. It has been observed that GAP cured with **4b** in absence of catalyst is very smooth and clean. Whereas, isocyanate based cured GAP showed voids and evaluation of gases.



GAP-DIOL Cured with N-100

GAP-DIOL Cured with 4b

Figure 5 GAP cured with isocynate and non-isocyanate under same experimental conditions

Further, experiments were carried out to see the difference between curing of GAP with conventional curator and non-isocyanate curator. GAP cured with isocyante (N-100) in presence of catalyst dibutyltindilaurate (DBTDL) at room temperature under moisture-free environmental condition. Similarly, GAP cured with non-isocyanate curator at room temperature without moisture control. The results of thermal and mechanical properties of cured samples were presented in **Table-5**. GAP cured with non-isocyanate curator revealed good mechanical properties such as tensile and E-mod as compared to GAP cured with isocyante (N-100). However, % of elongation degreases which could be optimized with varying amount of curator. GAP-aromatic bis(propargyl) ethers curing procedure appear to be simple and could be alternate to conventional isocynate based curing systems. In addition to this, these new non-isocyanate based curing system does not require catalyst, specific humidity control and also curing reaction occurs at relatively low temperature (30-50° C).

Table 5 Thermal and mechanical properties of GAP cured with isocyanate and non-isocyanate curing agents.

Cured polymer Samples*	DSC exothermic Energy release (Jg^{-1})	T_{max} (◦C)	E-Mod (kgf/cm^2)	Tensile (kgf/cm^2)	Max Force (kgf)	Elongation at Max (%)	Elongation (%)
GAP+N-100	2424	250	2.14	2.52	0.35	146.61	148.47
GAP + 4b	1499	258	83.8	36.49	9.52	47.60	47.78
GAP +4c	2260	257	58.3	18.66	5.18	35.71	35.84

*the mixture kept at room temperature for 2 days and post curing for 3 days at 50◦C

3 Conclusions

Bis-propargyl aromatic esters **2a-e** and ethers **4a-c** were successfully synthesized and fully characterized by FT-IR, NMR, MS and elemental analysis. Reverse phase HPLC analysis of the synthesized compounds showed purity >98%. GC-MS analysis of compounds **2a-e** and **4a-c** showed molecular ion peak M^+ at m/z in agreement with their molecular formula. The effects of temperature on curing reaction were studied independently for GAP-N100 and GAP-4b. The results are indicates that at room temperature (303 K) required 18-30 hrs for gel formation (gel point). It is clearly shown that gelling time of newly synthesized curator based binder system decreases as temperature is increases.

The influence of electron deficient group present in the curators was studied. The results indicated that curator having nitro group (**4c**) showed higher rate of reaction as compared curator without nitro group (**4b**). Further, activation energy for curing reaction of GAP-4b & GAP-4c systems are 15.56

& 13.22kcal/mol respectively, which is further evidence for effect of nitro group present in the curator. It has been observed that GAP cured with **4b** in absence of catalyst is very smooth and clean. Whereas, isocyanate based cured GAP showed voids and evaluation of gases.

The results of thermal and mechanical properties of GAP cured with N100 or non-isocyanate curators reveals that good mechanical properties as compared to conventional curing system. It has been demonstrated that GAP-aromatic bis(propargyl) ethers curing procedure appears to be simple and could be alternate to conventional isocynate based curing systems. In addition to this, these new non-isocyanate based curing system does not require any catalyst, specific humid control and also curing reaction occurs at relatively low temperature (30-50° C).

4 Experimental

Materials and methods

Raw materials like propargyl bromide (80% solution in toluene), potassium carbonate (anhydrous), resorcinol, hydroquinone, p-toluic acid, terephthalic acid, isophthalic acid were purchased from M/s Merck. GAP-diol (molecular weight~1800) was synthesized in lab. All reagents and chemicals used in the present study were of AR grade.

FT-IR spectra were recorded on Nicolet FTIR-5700 spectrophotometer using potassium bromide (KBr) matrix/ATR. ^{1}H and ^{13}C NMR spectra were recorded using Varian 300 MHz instrument in deuterated chloroform/dimethylsulfoxide (DMSO) where tetramethylsilane (TMS) was used as internal standard. Differential Scanning Calorimetery (DSC) was recorded on a DSC-7 Perkin Elmer instrument at heating rate of 10°C/min in nitrogen atmosphere. Elemental analysis was recorded using EA CHNS Model Vario Micro Cube. Gas chromatography-mass spectroscopy (GC-MS) studies were carried out on a Perkin Elmer, Clarus 500 instrument operating at source temperature 200 °C and helium is used as carrier gas. High performance liquid chromatography (HPLC) studies were undertaken on Ultimate_3000 Dionex HPLC system, at operating temperature 25°C by using reverse phase C-18 column (4mm x 250mm), mobile phase acetonitrile/water(60:40), flow rate 1 ml/minute, injection volume 10 μl in isocratic mode. GAP-propergyl ester/ether (30%. of GAP, w/w) without catalyst were mixed at room temperature. Curing of GAP with Desmodur N-100 was also carried out at room temperature in presence of catalyst dibutyltin dilaurate(DBTDL). FTIR spectra were recorded at different time intervals for both the samples and intensity of the absorption band were calculated by using OMNIC software. Mechanical properties, viz tensile strength, % elongation of the cured polymers were evaluated using Universal Testing Machine((Hounsfield, H25KS)

General procedure for synthesis of Bis(prop-2-ynyl)benzene dicarboxylate (2a-e)

Aromatic dicarboxylic acid (**1a-e**, 0.06 mol) was dissolved in 100 mL dimethyl formamide. To this solution, K_2CO_3 (0.14 mol) was added and stirred at 60°C for 30 min. Then propargyl bromide (0.15, mol) was added drop wise and reaction mixture was heated continuously at 60°C for 7-10 h. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled to room temperature and filtered. Filtrate was quenched with crushed ice and the solid separated was filtered, washed with cold water and dried. The crude products were purified by column chromatography using n-hexane/ethyl acetate as elute.

Bis(prop-2-ynyl)benzene-1,4-dicarboxylate (2a) :15.6 g , 54 % yield; white solid ; m.p. 110.5°C; R_f :0.72 (20 % EtOAc/n-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.55-2.56 (t, 2H, CH),4.96 (d,4H, CH_2), 8.15 (s,4H, aromatic) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$), δ: 52.83(CH_2), 75.36, 77.31(CH), 129.84, 133.51(aromatic), 164.93(C=O)ppm; IR (KBr) ν :3250, 3120, 2937, 2870, 2127, 1716,1267, 653 cm^{-1}; GC-MS (EI, 70 eV) m/z: 242 [M^+]; Elemental Anal. calcd (%) for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13; Found : C, 69.14; H, 4.08.

Bis(prop-2-ynyl)-2-nitrobenzene-1,4-dicarboxylate (2b): 1.67g, 61 % Yield; white solid; m.p. 88.38 °C; R_f: 0.61 (20 % EtOAc/n-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.60-2.61 (t, 2H, CH), 4.95-4.99 (dd, *J*=10.40, 2.47 Hz, 4H, CH_2), 7.82-7.85 (d,1H, Ar), 8.35-8.38 (dd, *J*=7.96, 1.64 Hz,1H, Ar), 8.62 (s,1H, Ar) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ:52.77(CH_2), 75.30, 77.38(CH), 128.79, 129.97,131.11, 134.37(aromatic), 164.84(C=O) ppm; IR (KBr) ν: 3279, 3117,3059 ,2939, 2883, 2133, 1732, 1616, 1539, 1363,1226, 1062, 655 cm^{-1}; GC-MS (EI, 70 eV) m/z: 287 [M$^+$]; Elemental Anal. calcd (%) for $C_{14}H_9NO_6$: C, 58.53; H, 3.13;N, 4.87 Found : C, 58.18; H, 2.95; N: 4.86.

Bis(prop-2-ynyl)-3,5-dinitrobenzene-1,4-dicarboxylate (2c): 1.62, 62% Yield; cream solid; m.p. 89.98 °C; R_f: 0.9 (20 % EtOAc/n-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.62-2.63 (t, *J*=2.48 Hz, 2H, CH), 5.05-5.06(d,4H, CH_2), 9.23-9.24(t,2H, Ar) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ: 54.04(CH_2), 76.37, 77.25(CH), 122.70, 129.56, 132.99, 148.65(aromatic), 161.80(C=O) ppm; IR (KBr) ν: 3290, 3088, 2947, 2885, 2135, 1731, 1626, 1593, 1542, 1345, 1274, 1163, 1001, 962, 651 cm^{-1}; MS (EI): m/z : 331.9 [M$^+$].

Bis(prop-2-ynyl) benzene-1,3-dicarboxylate (2d):12.46 g, 85 % Yield; white solid; m.p. 85.53°C; R_f: 0.78 (20 % EtOAc/n-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.54-2.56 (t, *J*=2.47 Hz, 2H, CH), 4.95-4.96(d, *J*=2.44 Hz, 4H, CH_2), 7.56-7.59(t,1H, Ar), 8.25-8.29(dd, *J*=7.81, 1.73 Hz,2H, Ar), 8.73 (s,1H, Ar) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ: 53.57, 54.08(CH_2), 76.20, 77.31(CH), 125.32, 130.15, 133.08, 134.05(aromatic), 162.85, 163.94(C=O) ppm; IR (KBr) ν: 3265, 3086,2943, 2874, 2129, 1716, 1607, 1236, 1084,653 cm^{-1}; GC-MS (EI, 70 eV) m/z: 242 [M$^+$]; Elemental Anal. calcd (%) for $C_{14}H_{10}O_4$: C, 69.42; H,4.13 Found :C,69.10; H, 4.03.

Bis(prop-2-ynyl)-5-nitrobenzene-1,3-dicarboxylate (2e): 3.9 g, 70 % Yield; white solid; m.p. 145.54 °C; R_f: 0.74 (20 % EtOAc/n-hexane); ^{1}H-NMR(300 MHz,$CDCl_3$)δ: 2.59-2.61 (t,2H, CH), 5.02-5.03 (d, *J*=2.49 Hz, 4H, CH_2), 9.02-9.08(d,3H, Ar)ppm; ^{13}C-NMR (300 MHz, $CDCl_3$)δ: 53.79)CH_2), 76.02, 77.67(CH), 128.71, 131.92, 136.13, 148.51(aromatic), 162.89(C=O); IR(KBr) ν : 3286, 3090, 2922, 2852, 2131, 1716, 1607, 1236, 1084, 653 cm^{-1}; GC-MS (EI, 70 eV) m/z: 287 [M$^+$]; Elemental Anal. calcd (%) for $C_{14}H_9NO_6$: C, 58.53; H, 3.13;N, 4.87 Found**:** C, 58.51; H: 3.06; N, 4.91.

General procedure for synthesis of bis(2-propynyloxy) benzene (4a-c)

Mixture of aromatic dihydroxybenzene (**3a-c**, 0.064 mol) and potassium carbonate (0.14 mol) was stirred in 60 mL dimethylformamide/acetone at 60^{0}C for 30 min. Then propargyl bromide (0.15,mol) was added drop wise and reaction mixture heated at 60^0C for 5-10 h. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled to room temperature and filtered. Filtrate was washed with water followed by brine. Extract was dried over sodium sulfate and concentrated on rotary evaporator. Thick brown mass was collected, purified by column chromatography using 5 % ethyl acetate in n-hexane.

1,3-Bis(2-propynyloxy)benzene (4a): 7.74 g, 47 % Yield; amber colored solid; m.p. 40.69 $^\circ$C; R_f: 0.82 (20 % EtOAc/n-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.53-2.55 (t, *J*=2.41 Hz, 2H, CH), 4.68-4.69 (d, *J*=2.44 Hz, 4H, CH_2), 6.62-6.65 (m,3H, aromatic), 7.23 ppm (s,1H, aromatic); ^{13}C-NMR (300 MHz, $CDCl_3$)δ:55.97(CH_2), 75.80, 78.60(CH), 102.56, 108, 130.10, 158.84(aromatic) ppm; IR (KBr) ν: 3289, 3073, 2919, 2867, 2121, 1593, 1086,682 cm^{-1}; GC-MS (EI, 70 eV) m/z:186 [M^+]; Elemental Anal. calcd(%) for $C_{12}H_{10}O_2$: C, 77.41; H, 5.37 Found : C, 77.44; H, 5.28.

1,4-Bis(2-propynyloxy)benzene (4b): 9.33 g, 56 %Yield; cream solid; m.p. 48.92 $^\circ$C; R_f : 0.8 (20 % EtOAc/n-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.52-2.53 (t, *J*=2.41 Hz, 2H,CH), 4.65-4.66 (d, *J*=2.38 Hz, 4H, CH_2), 6.94 (s,4H, aromatic) ppm; ^{13}C-NMR (300 MHz, $CDCl_3$) δ: 56.19(CH_2), 75.37, 78.65(CH), 115.77, 152(aromatic) ; IR (KBr) ν: 3289, 3049, 2921, 2864, 2120, 1593, 1031, 640 cm^{-1}; GC-MS (EI, 70 eV) m/z:186 [M^+]; Elemental Anal. calcd (%) for $C_{12}H_{10}O_2$: C, 77.41; H, 5.37 Found : C: 77.29; H, 5.20.

1,4-Bis(2-propynyloxy)-2-nitrobenzene(4c): 4.8 g, 46 % Yield; Light yellow solid ; m.p.76.31^{0}C; R_f:0.57 (20%EtOAc/n-hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 2.57-2.58(m, 2H, CH),4.69-4.78 (m,*J*=2.37 Hz,4H, CH_2), 7.19-7.23 (m, 2H, aromatic),7.47 (d,1H, aromatic)ppm; ^{13}C-NMR (300 MHz, $CDCl_3$)δ:56.57, 58.05(CH_2), 76.45, 77.47(CH), 111.60, 117.78, 121.24, 140.36, 145.45, 151.47(aromatic) ppm; IR (KBr) ν: 3284, 3101,2926, 2863, 2129, 1579,1529,1344, 1016, 650 cm^{-1}; GC-MS (EI, 70 eV) m/z:231[M^+]; Elemental Anal. calcd (%) for $C_{12}H_9NO_4$: C, 62.33; H,3.89; N,6.06 Found: C, 62.13; H, 3.80; N, 5.99.

General procedure for nitration of dicarboxylic acids

100 mL oleum (18 %) transferred to 500 mL three necked round bottom flask, 75 mL fuming HNO_3 (98 %) mixed at temperature below 25°C. To this nitrating mixture 25g corresponding dicarboxylic acid (1a,1d)/ p-toluic acid was added slowly maintaining same temperature. Temperature of reaction mixture was slowly raised to 90°C and maintained temperature for 4 hrs. Then reaction mixture cooled to room temperature and poured into the 500 g crushed ice white compound separated, filtered, washed with water till acid free. It was purified by recrystallization from water to give white crystals.

Synthesis of 3,5-Dinitrobenzene-1,4-dioic acid (1c)

40 mL H_2SO_4 transferred to 250 mL three necked round bottom flask and 5 g (0.02 mol) 3,5-dinitro-p-toluic acid was added. To this reaction mixture 15 g (0.05 mol) sodium dichromate dihydrate was added in portions maintaining temperature between 35-40 °C. After completion of addition reaction mixture stirred for 2 h at 40 °C temperature, kept overnight and poured into crush ice (200g). Cream colored product separated, filtered and washed with cold water. Compound purified by recrystallization from ethyl alcohol to give white crystals.

2-Nitrobenzene-1,4-dioic acid(1b) : 27.2 g, 85 % Yield; White solid; m.p. 275 °C; ^{1}H-NMR (300MHz, DMSO-d_6) δ, 7.95-7.97 (d, *J*=7.93 Hz, 1H), 8.27-8.28 (dd, *J*=7.93, 1.61 Hz, ,1H), 8.37 (m,1H); IR (KBr) ν: 3088, 1705, 1624, 1543,1336 cm^{-1}. Elemental Anal. calcd (%) for $C_8H_5NO_6$: C, 45.49; H,2.36; N,6.63 Found: C, 45.11; H, 2.37; N, 6.52.

4-Methyl-3,5-dinitrobenzoic Acid : 29.50 g**,** 88 % Yield; White solid; m.p 159 °C; ^{1}H-NMR (300 MHz, DMSO-d_6), δ: 8.57(s, 2H), 2.50 (s,3H) ppm; IR (KBr) ν: 3082, 2877, 2831, 1703, 1631,1541, 1350 cm^{-1}. Elemental Anal. calcd (%) for $C_8H_6N_2O_6$: C, 42.47; H, 2.65; N, 12.38 Found: C,42.38; H, 2.63; N, 12.38.

3,5-Dinitrobenzene-1,4-dioic acid(1c) : 3.9 g, 69 %Yield; White solid; m.p. 279 °C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 8.77(s, 2H) ppm; IR (KBr) ν: 3099, 1714, 1622,1546,1346 cm^{-1}. Elemental Anal. calcd (%) for $C_8H_4N_2O_8$: C, 37.50; H, 1.56; N,10.93 Found: C,37.26; H,1.60; N, 10.73.

5-Nitrobenzene-1,3-dioic acid(1d) : 21.17 g, 83 % Yield; White solid; m.p 264 °C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 8.66-8.69 ppm (d,3H); IR(KBr) ν: 3545, 3462, 3007, 1703, 1626, 1541, 1352 cm^{-1}.

2-Nitrobenzene-1,4-diol (3c) : 7.99, 60 % Yield ; Orange solid; m. p : 133 °C; ^{1}H-NMR (300 MHz, DMSO-d_6) δ: 10.19 (s,1H), 9.65(s,1H), 7.56(d,1H), 6.97-7.07 (m,2H)ppm, (After D_2O Exchange : 7.05-7.16(d,1H), 6.74-6.92 (m,2H)ppm; IR (KBr) ν: 3458, 3084,1622, 1587, 1332 cm^{-1}. Elemental Anal. calcd (%) for $C_6H_5NO_4$: C, 46.45; H, 3.22; N, 9.0 Found: C,46.21; H, 3.15; N, 8.93. GC-MS (EI, 70 eV) m/z: 155 [M$^+$].

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Supporting Information

All the spectral data for characterization of the compounds are provided.

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Table of Contents

Synthesis of Bis(propargyl) Aromatic Esters and Ethers: A Potential Replacement for Isocyanate Based Curators

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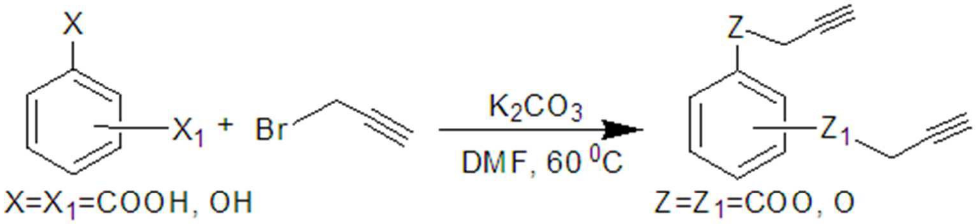

8 examples, Yield %:46-85, Envirinmental benign