

## Influence of Chain Length of Diol on the Swelling Behavior of Citric Acid Based pH Sensitive Polymeric Hydrogels: A Green Approach

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**ABSTRACT:** Synthesis of pH-sensitive hydrogels of citric acid with varying diol units *viz.*, 1,2 Ethane diol, 1,4 butane diol, and 1,6 hexane diol along with methacrylic acid towards the solventless green approach. The formations of the hydrogels were identified using FTIR spectroscopy. Thermal characterization (thermo gravimetric analysis, differential thermal analysis (DTA), and differential scanning calorimetry) and morphology of the synthesized hydrogels have been investigated. Swelling studies of hydrogels in various pH ranging from 4.0 to 10.0 have been investigated. The results of the swelling studies implied that percentage of swelling comparatively higher at neutral pH (7.4) than at acidic and alkaline pH. The inverse relationship was noticed, where ascending the diol units of hydrogel in swelling equilibrium. The hydrogels with the increasing chain length show a noticeable pH sensitivity and which could be considered as smart hydrogel. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41403.

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### INTRODUCTION

Polymeric hydrogels have an important role in many technological areas such as drug delivery, sensors, absorbent materials, pharmaceutical fields, medicines, biotechnology, and agriculture. Hydrogels are the three-dimensional polymeric network, which consist of hydrophilic polymeric network that constituted by chemical/physical cross-linking, hydrophobic, or hydrogen bonded interaction. They are gifted for absorbing large quantities of water, saline, or physiological fluid without being dissolved.<sup>1,2</sup> Hydrogels behave similar to natural tissue, due to their soft and fragile nature. Excellent hydrophilicity and biocompatibility of hydrogels contributed towards the fast development materials of various biomedical applications. The major advantage of pH-responsive polymeric hydrogels is that they offer a number of eco-friendly applications such as metal ion removal, dye removal, and so forth. They are desirable for biomedical applications that can control drug, peptide, or protein release, and so forth.<sup>3–5</sup> The “smart” hydrogels have been broadly studied due to their response to the stimuli-sensitive changes in environmental conditions. They can display swelling transition behavior owing to the variations in pH, ionic strength, and temperature. Among all types of intelligent hydrogels, much attention has been devoted on pH sensitive hydrogels because of their potential usage in the field of

pharmaceutical, medicine, biotechnology, and agriculture and food industry, and so forth, and mainly in the drug delivery systems.

pH sensitive hydrogels are polymer networks that have pendant acidic and basic functional groups which either accept or release protons as a result of changing external pH. They are designed by acidic or basic functional groups which are present on the polymer network. These materials retain water due to the presence of hydrophilic functional groups, such as hydroxyl, carboxyl, amide, sulfonyl, and so forth, represented in the polymer chains.<sup>6,7</sup> In the last decades, several works have been explored on the feasibility of pH sensitive hydrogels and their synthesis using acrylic acid or methacrylic acid or acrylamide.

Recently polymers based on citric acid received significant attention in various biomedical and eco-friendly applications. Citric acid is an economical and multifunctional monomer and mainly used to participate ester crosslinking formation. Further, it provides hydrogen bonding and other binding sites for bio conjugation.<sup>8</sup> Conversely, a relatively new type of pH sensitive polymer hydrogel was synthesized and investigated for their swelling and thermal properties.<sup>9</sup> Barroso-Bujans et al. had fabricated that the oligomers composed of citric acid with ethylene glycol and long-chain aliphatic alcohols by polycondensation with biomedical applications.<sup>10</sup> Another approach to formulate

**Table I.** Physical Parameter of Series of Polymeric Hydrogels of Various Diol

S. No	Sample	Composition (mol)					Color, appearance and solubility
		MAA	CA	ED	BD	HD	
1	MACED	0.025	0.025	0.025	-	-	White glassy gel, insoluble in water
2	MAC1ED4	0.025	0.010	0.040	-	-	White glassy gel, insoluble in water
3	MAC2ED3	0.025	0.020	0.030	-	-	White glassy gel, insoluble in water
4	MAC3ED2	0.025	0.030	0.020	-	-	White glassy gel, insoluble in water
5	MACBD	0.025	0.025	-	0.025	-	White glassy gel, insoluble in water
6	MAC1BD4	0.025	0.010	-	0.040	-	White glassy gel, insoluble in water
7	MAC2BD3	0.025	0.020	-	0.030	-	White glassy gel, insoluble in water
8	MAC3BD2	0.025	0.030	-	0.020	-	White glassy gel, insoluble in water
9	MACHD	0.025	0.025	-	-	0.025	White glassy gel, insoluble in water
10	MAC1HD4	0.025	0.010	-	-	0.040	White glassy gel, insoluble in water
11	MAC2HD3	0.025	0.020	-	-	0.030	White glassy gel, insoluble in water
12	MAC3HD2	0.025	0.030	-	-	0.020	White glassy gel, insoluble in water

citric acid-based copolymer with excellent biocompatible hybrid materials which can act as a Nano medicine.<sup>11</sup> Namazi and Adeli contributed towards novel linear-globular thermoreversible hydrogel ABA type copolymers from dendritic citric acid as the A blocks and poly (ethylene glycol) as the B block with drug delivery applications.<sup>12</sup> Liu et al. developed poly(glycerine citrate) for drug delivery applications (drug theophylline).<sup>13</sup> Gyawali et al. derived citric acid constructed cross-linked polymer for cell delivery.<sup>14</sup> Tuncer Caykara contributed pH-sensitive hydrogels of *N*-vinyl 2-pyrrolidone/citric acid for various environmental applications *viz.*, metal ion removal and dye removal.<sup>15</sup> Yao et al. combined synthetic and natural polymers with maintaining favorable properties (biodegradation, bioactivity, and pH-sensitivity).<sup>16</sup>

Ethane diol (ED) and their homolog (BD and HD) were chosen as a difunctional monomer to improve the properties of hydrogels because of its flexibility and biocompatibility.<sup>17</sup> Zuber and coworkers prepared surface characteristics of biocompatible blends based on chitin/1,4-butane diol.<sup>18,19</sup> Madras and coworkers investigated the effects of hexane diol in the preparation of poly(trimethylol propane triacrylate)/poly(hexane diol diacrylate) interpenetrating polymer network used for the fabrication of microgear, micro cantilever applications.<sup>20</sup>

Methacrylic acid (MAA) is an effective monomer to develop the pH responsive polymeric hydrogels because of its excellent biocompatibility, non-toxic, and so forth, they can easily be blended or compounded with other monomers to trigger pH stimuli responsive properties. Numerous amount of work has been contributed by Peppas et al. on pH responsive hydrogels based on MAA for biochemical and biomedical applications such as biosensors, membranes, molecular imprinting, drug delivery devices, and so forth.<sup>21–25</sup>

Green Chemistry aimed to focus greater alternative for toxic solvents, minimizing the synthesis procedure and simplified purification techniques.<sup>26</sup> In recent years, solvent-free reaction has drawn a considerable attention and popularity. Functionali-

zation performed under solventless conditions has greater improvement in the designing of green process with many applications.

Hence, the present investigation aimed to synthesize pH sensitivity of the polymeric hydrogel under solventless conditions using greener approach. Further, influence of chain length of the diol on swelling behavior has been deliberated exclusively. In addition, spectral, morphology, and thermal investigation have also been investigated.

## EXPERIMENTAL

### Materials and Methods

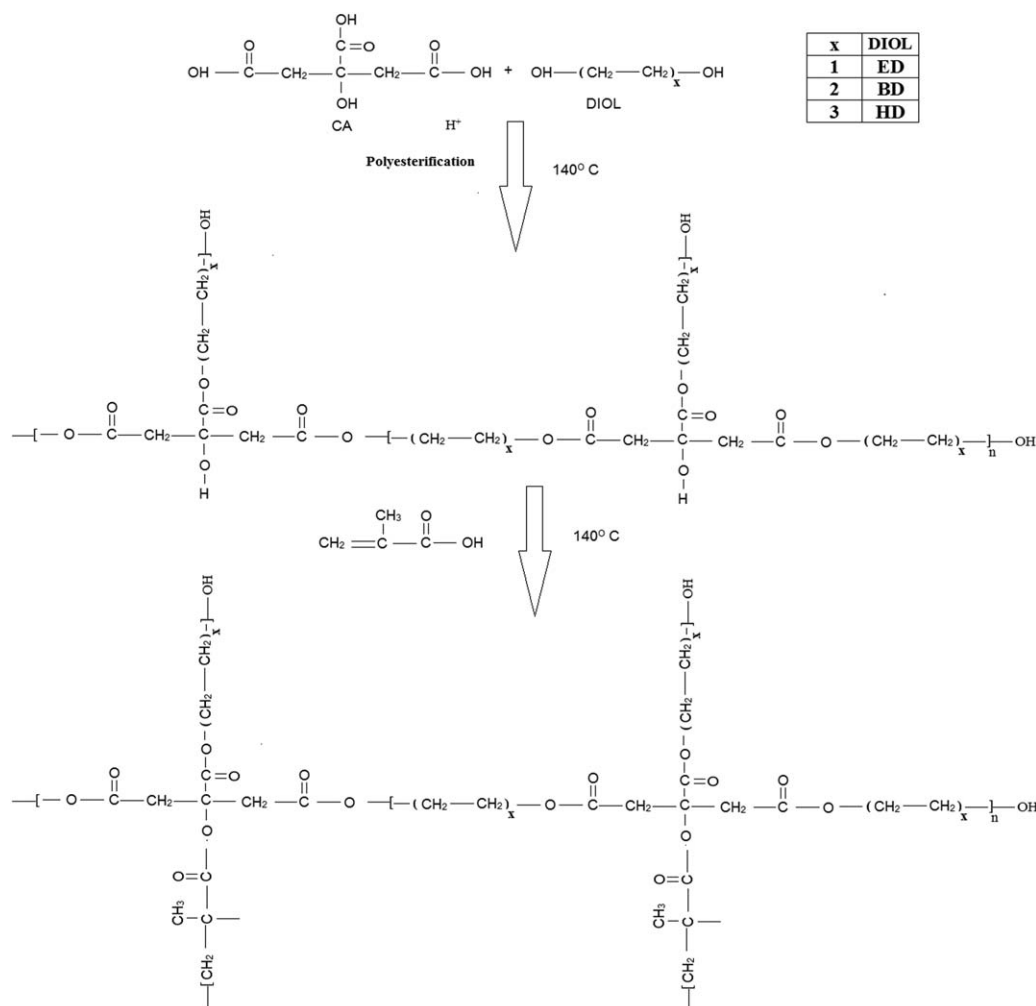
1,2 Ethane diol (ED), 1,4 butane diol (BD), and 1,6 hexane diol (HD) were purchased from Merck (India). The monomer(s), anhydrous citric acid (CA) and methacrylic acid (MAA), were purchased from Sigma Aldrich Chemical Company (Bangalore, India). Prior to use, MAA was vacuum distilled at 54°C/25 mmHg to remove the inhibitor hydroquinone. Double distilled water was used throughout the experiments.

### Synthesis of Polymeric Hydrogel MACED, MACBD, and MACHD

Synthesis of hydrogel involved in two steps according to our previous contribution.<sup>9</sup> In brief, esterification was performed among citric acid and various diols (ED, BD, and HD) in nitrogen atmosphere at 140°C resulted pre-polyester chains by formation pre-polyester (CED, CBD, and CHD). Further, methacrylic acid (0.025 mol) was also added to pre polyester (CED, CBD, and CHD) at 140°C with constant stirring for 2 h in the inert atmosphere. The formation of glassy gel (MACED, MACBD, and MACHD) infers the completion of the reaction. The description of the ED, BD, and HD-based hydrogels was presented in Table I. The general mechanism of the formation of polymeric hydrogel was given in Scheme 1.

### FTIR Studies

FTIR spectra of polymeric hydrogels were recorded in KBr pellets on FTIR-8400 S, Shimadzu spectrophotometer. Spectra were



**Scheme 1.** Synthetic pathway of polymeric hydrogels of citric acid/methacrylic acid with various diols.

recorded over the wavelength range between 4000 and 400  $\text{cm}^{-1}$ .

### Swelling Studies

Swelling of the polymeric hydrogels was performed in triplicate by gravimetric method. A known weight of dried hydrogels was immersed in phosphate buffer solutions (PBS) of various pH ranging from 4.0 to 10.0 for 6 h in the periodical interval of 0.5 h and wiped with tissue paper to remove the excess solvent. Weighed the gel and placed in the same bath for another cycle. The same procedure was conducted for the solutions with different pH values (4.0–10.0) which were modified using aqueous HCl and NaOH solution. The pH values were precisely checked with a pH meter (Systronics 3300, India), known amounts of the dried hydrogel were immersed in solutions of different pH and the swelling degree and equilibrium swelling were calculated with eqs. (1) and (2).

$$S\% = \frac{W_t - W_d}{W_d} \times 100 \quad (1)$$

$$S_{eq}\% = \frac{W_{eq} - W_d}{W_d} \times 100. \quad (2)$$

$W_t$  and  $W_{eq}$  are the weights of the sample in the dried state, swollen state at time “ $t$ ” and swollen at equilibrium, respectively. The

values of  $S\%$  increased with time, but reached constant value. This value of swelling was called equilibrium swelling ( $S_{eq}\%$ ).

### Scanning Electron Microscopy

Scanning electron micrographs of the dried polymeric hydrogel samples were performed using Hitachi, Model: S-3400. The synthesized hydrogels were subjected to gold sputtering under vacuum before use. A remarkable three-dimensional appearance with high resolution was obtained in the polymer hydrogels.

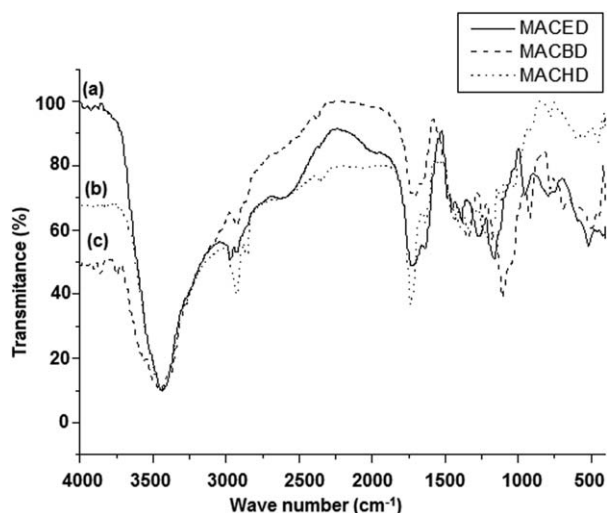
### Thermal Analysis

Differential scanning calorimetry (DSC) using a Q20 DSC Differential Scanning Calorimeter (TA Instruments) and thermo gravimetric analysis (TGA) using an SDT Q 600 Simultaneous DSC–TGA (TA Instruments) were used to examine the thermal properties of polymeric hydrogels. The glass transition temperatures of the hydrogels were determined by differential scanning calorimetry. Both TGA and DSC curves were recorded in the temperature range of ambient to 500°C at a heating rate of 10°C  $\text{min}^{-1}$ , under  $\text{N}_2$  atmosphere.

## RESULTS AND DISCUSSION

### FTIR Spectral Studies of Polymeric Hydrogels

Infrared spectroscopy was performed to illustrate the chemical structure and nature of bonding formed within the hydrogel.

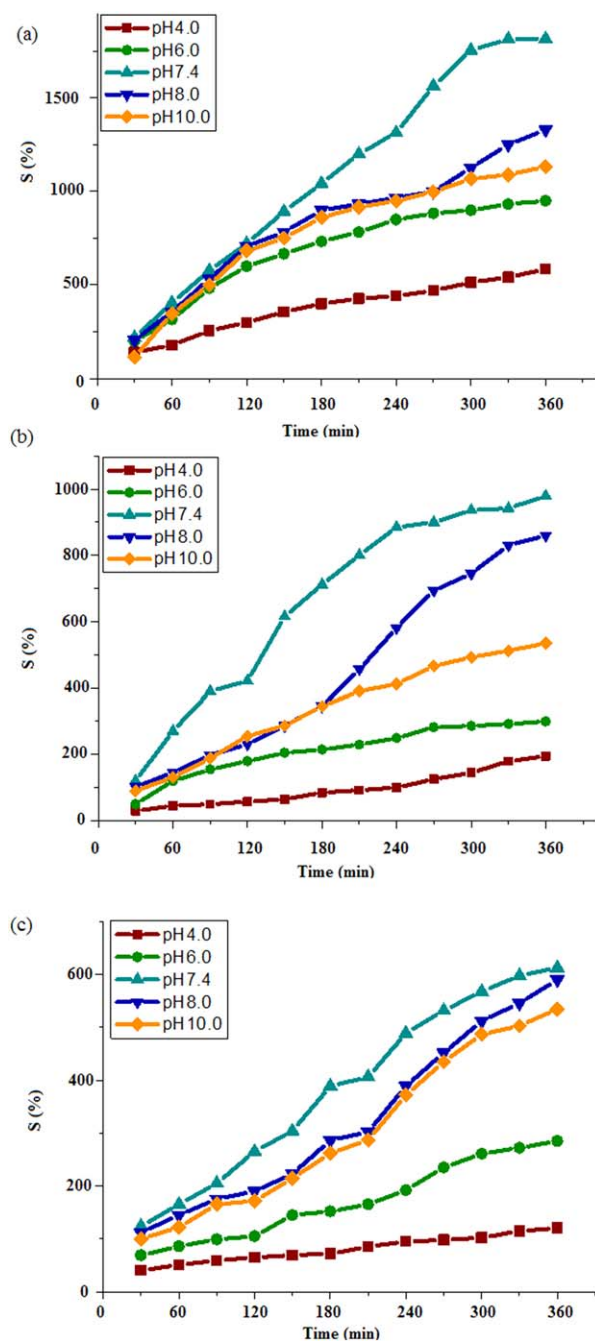


**Figure 1.** Comparative FTIR spectra of (a) MACED, (b) MACBD, and (c) MAHD.

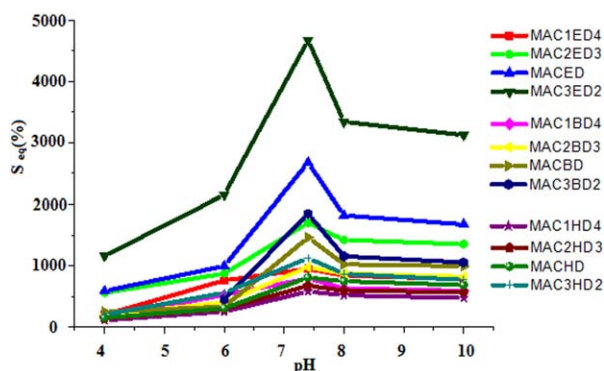
The FTIR spectra of the MACED were shown in Figure 1(a), the most distinct peak  $1719\text{ cm}^{-1}$  which can be ascribed to the band C=O stretching.<sup>25</sup> The C—O stretching vibration observed at  $1166.91$  and  $1269.64\text{ cm}^{-1}$ .<sup>27</sup> It is clearly indicated the formation ester by utilization of the citric acid unit involved reaction with diol units. The —C—H symmetric stretching vibration occurs at  $2907.41$  and  $2926.60\text{ cm}^{-1}$ . The new absorption peaks observed at  $1449.86\text{ cm}^{-1}$  assigned to stretching vibration of  $\text{COO}^-$ . The FTIR transmittance spectra of MACBD hydrogels were shown in Figure 1(b). The spectra showed strong bands at  $1718.71$  and  $1041.64$  and  $1107.66\text{ cm}^{-1}$  were attributed to C=O and C—O—C stretching, respectively. The peak at  $2927.83$ ,  $2864.03\text{ cm}^{-1}$  corresponds to stretching vibration of the methylene group of polymer backbone. In addition, the absorption peaks at  $1431.54$  and  $1349.68\text{ cm}^{-1}$  assigned to the stretching of  $\text{COO}^-$  appeared in the spectrum of MACBD hydrogels. The spectral characteristics of MACHD hydrogels were presented in Figure 1(c). According to the figure, the C=O stretching vibration of ester carbonyl groups has appeared at  $1737.29\text{ cm}^{-1}$ . The stretching vibration of C—O observed at  $1077.59$ ,  $1026.02$ , and  $1115.70\text{ cm}^{-1}$ . In addition, the characteristic absorption band of  $\text{COO}^-$  was observed in  $1400.64$ ,  $1350.32\text{ cm}^{-1}$ . An absorption band with a weak shoulder peak around  $2927.07$ ,  $2858.00\text{ cm}^{-1}$  which correspond to the stretching of aliphatic C—H groups, respectively.

MACED, MACBD, and MAHD hydrogels were exhibited  $\text{COO}^-$  stretching at  $1449.80$ ,  $1449.10$ , and  $1447.52\text{ cm}^{-1}$ , respectively. An almost similar observation has been reported by Fu and coworkers at  $1442\text{ cm}^{-1}$  for their carboxymethyl cellulose (CMC) hydrogels.<sup>28</sup> Similar to our observation, Wang et al. reported  $\text{COO}^-$  stretching at  $1454\text{ cm}^{-1}$  for their pH-sensitive hydrogel composed of sodium alginate-*g*-poly(sodium acrylate) network and linear polyvinylpyrrolidone (PVP) systems.<sup>29</sup> These results clearly indicated the formation hydrogels. According to Guillermo and coworkers, the hydrogen bonded hydroxyl group can contribute to improve hydrophilicity, biocompatibility, and

mechanical properties of the polymer.<sup>30</sup> In addition, there also a distinct broad absorption band on MACED was observed at  $3438.00\text{ cm}^{-1}$  can be attributed to the hydrogen bonded hydroxyl groups. Similarly, MACBD showed a broad band around  $3280.00$ – $3650.00\text{ cm}^{-1}$  which clearly marked the presence of the hydrogen bonded hydroxyl group. A broad absorption band of —OH in the range of  $3400.00$ – $3700.00\text{ cm}^{-1}$  appeared in MACHD spectrum. These hydrogen bonded



**Figure 2.** The swelling percentage of (a) MACED, (b) MACBD, and (c) MACHD-based hydrogels at different pH with respect to time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 3.** The swelling equilibrium of series of hydrogels of various diol (ED, BD, and HD) at pH 4.0, 6.0, 7.4, 8.0, and 10.0. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

hydroxyl groups tune the biocompatibility and other extraordinary properties.

### Swelling Studies of Polymeric Hydrogels

The dynamic swelling behavior of dried hydrogels was described by a function of the time of immersion in swelling medium of varying pH (4.0, 6.0, 7.4, 8.0, and 10.0). Swelling property of polymeric hydrogels can be influenced by pH of the immersion medium.<sup>31</sup> As hydrogels were composed of the acidic group which can be dissociated or get protonated at some suitable pH of swelling media, the  $S\%$  underwent an appreciable change with external pH. Swelling of hydrogels sharply changes in the vicinity of their  $pK_a$  and  $pK_b$  values.<sup>32</sup> It is well known that CA is a triprotic acid with dissociation constant  $pK_{a1} = 2.94$ ,  $pK_{a2} = 4.14$ ,  $pK_{a3} = 5.82$ <sup>33</sup> and dissociation constant of methacrylic acid found to have a value of 4.66. Active swelling was observed only when the pH of the swelling medium crossed over the  $pK_a$  value of the concerned hydrogels which facilitated a more hydrophilic nature and contributed to increased water absorption by formation carboxylate ion from hydrogel. At a low pH, complexation occurred, resulting in dropping the percentage of swelling.<sup>26</sup> This hydrogen-bonded complex causes the polymer network to be less hydrophilic.

As shown in Figure 2(a), the  $S\%$  of MACED hydrogel was strongly influenced by changes in the pH of the swelling medium. The MACED hydrogel showed  $S\%$  values after 6 h was found to be 585.00, 950.00, 1815.00, 1330.00, and 1133.00% at pH 4.0, 6.0, 7.4, 8.0, 10.0, respectively. It clearly indicated that  $S\%$  of MACED hydrogel progressively increases with respect to time and pH. It is obvious that  $S\%$  of MACED was significantly higher at neutral pH, compared to lower and higher pH value. A similar tendency was observed for both MACBD [Figure 2(b)] and MACHD [Figure 2(c)] polymeric hydrogels. The  $S\%$  of MACBD hydrogels at pH 4.0, 6.0, 7.4, 8.0, and 10.0 found to have 195.00, 300.00, 985.00, 860.00, and 943.20%. The MACHD hydrogel swelling percentage was found to have 100.00, 285.00, 613.20, 590.00, and 535.00%, respectively, at pH (4–10). As far as swelling results were concerned, it can be concluded that the swelling behavior of synthesized hydrogels mainly depends on the pH of the swelling medium.

It was obvious that the water absorbency was significantly higher for polymer hydrogels with  $pH > 4$ . As the pH value of

the medium increased from 4 to 7.4, a greater number formation of carboxylate ion ( $\text{COO}^-$ ) was formed because of many hydrogen bonds were broken and the electrostatic repulsion of anionic groups increased deeply in the polymer backbone of the hydrogels causes an increase in swelling.<sup>34,35</sup> The maximum swelling capacities were observed at pH 7.4, which might be attributed to the fact that hydrogel could swell more easily in the high osmotic pressure because of the ionic strength of external solution. Further, the increased pH value from 8.0 to 10.0 the swelling ability of the hydrogel dropped sharply. It may be due to screening effect of the counter ions ( $\text{Na}^+$ ). In fact, at high and low pH, the presence of high concentrations of the ions results in high ionic strength. When the ionic strength of the solution is increased, the difference in osmotic pressure between the hydrogel and the medium is decreased. Thus, the swelling capacity of the hydrogel is decreased.<sup>36,37</sup>

### Equilibrium Swelling Studies of Polymeric Hydrogels

To find out pH-response of a series of dried hydrogels were allowed to swell and reach swelling equilibrium in phosphate buffer solutions of varying pH at room temperature. At each of pH values, the equilibrium swelling  $S_{eq}\%$  at various pH was determined according to eq. (2). The swelling equilibrium  $S_{eq}\%$  was plotted as a function of pH shown in Figure 3, it was observed that the time taken to reach swelling equilibrium the hydrogel varied with different pH 4.0–10.0. The MACED hydrogels showed pH dependencies of equilibrium swelling revealed maxima at pH 7.4 than acidic and alkaline pH. The  $S_{eq}\%$  value of MACED at pH 4.0, 6.0, 7.4, 8.0, and 10.0 was corresponded to 587.00, 991.50, 2762.00, 1816.00, and 1675.00%, respectively. MACBD hydrogel showed the  $S_{eq}\%$  at pH 4.0, 6.0, 7.4, 8.0, and 10.0 found to have 250.00, 330.50, 1460.00, 1025.00, and 991.50%, respectively. The value of MACHD hydrogel exhibited  $S_{eq}(\%)$  of 150.00, 303.10, 808.40, 745.00, and 685.00% at pH 4.0, 6.0, 7.4, 8.0, and 10.0, respectively. Similar to our results Erici<sup>27</sup> has prepared pH-sensitive dextran-poly (MAA) based hydrogels with varying composition showed swelling equilibrium at pH 7.4 in the range of 40–1130%. MAC4ED1, MAC4BD1, and MAC4HD1 polymeric hydrogels were found to have an excellent swelling capacity at various pH. Finding from our observations that the increased composition of CA in hydrogel was found to enhance the swelling equilibrium. Summary of the equilibrium swelling of series of hydrogels is presented in Table II. The  $S\%$  increases with increasing pH of the medium, the swelling capacity was also increased. The MACED, MACBD, and MACHD hydrogels were showed equilibrium swelling 2762.00, 1466.00, and 808.40% at pH 7.4 might be attributed to the fact that hydrogel could swell more easily in the high osmotic pressure because of the ionic strength of external solution. However, as the pH further increased, the swelling capacity of the hydrogel decreased sharply. At pH 10.0, the observed  $S_{eq}\%$  values of MACED, MACBD, and MACHD were 1675.00, 916.60, and 685.00%, respectively, which was lower than observed results at pH 7.4.

There are two stand out for the increased swelling behavior of hydrogel as follows: (a) the observed increase in the swelling equilibrium with an initial increase in the hydrogel content of citric acid increases, the number of  $\text{—COO}^-$  groups along the

**Table II.**  $S_{eq}$ % Values of Methacrylic Acid-Based Citric Acid Containing Polymeric Hydrogels of Various Diol

S. No	Sample code	pH				
		4	6	7.4	8	10
1	MAC1ED4	200.00	757.00	950.00	840.00	780.00
2	MAC2ED3	560.00	869.00	1700.00	1420.00	1350.00
3	MACED	587.00	994.50	2676.20	1816.00	1675.00
4	MAC3ED2	1160.00	2150.00	4673.00	3340.00	3120.00
5	MAC1BD4	150.00	525.00	790.00	630.00	590.00
6	MAC2BD3	193.20	405.3	975.00	874.00	819.00
7	MACBD	250.00	330.50	1460.00	1025.00	991.00
8	MAC3BD2	475.00	450.30	1847.00	1154.00	1053.00
9	MAC1HD4	112.00	250.00	580.00	520.00	473.20
10	MAC2HD3	142.00	295.00	672.00	595.00	565.00
11	MACHD	150.00	303.00	808.00	745.00	685.00
12	MAC3HD2	200.00	556.20	1123.00	868.00	768.00

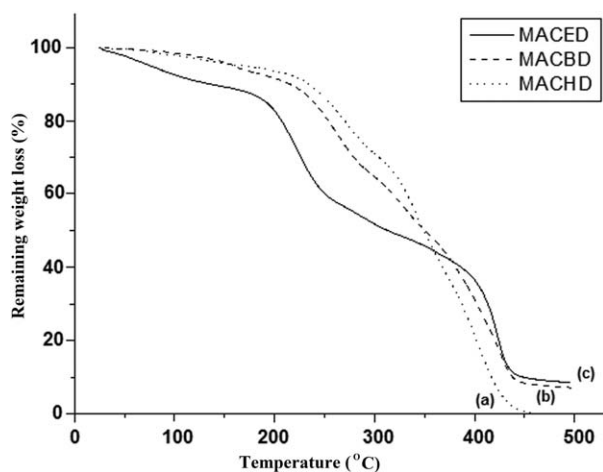
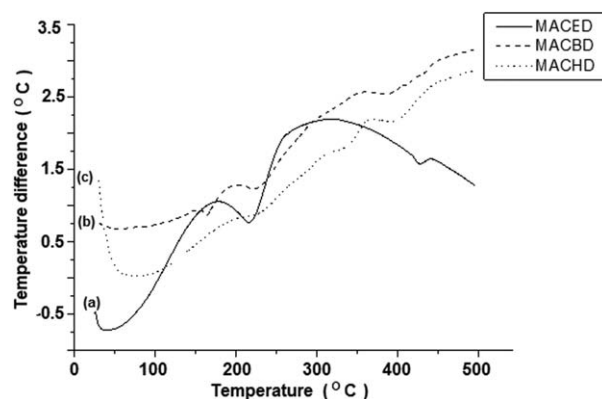
macromolecular chains also increases along with an increase in the number of free  $H^+$  ions (counter ions) within the gel phase. This causes an enhancement in the chain relaxation owing to the repulsion among similarly charged  $-COO^-$  groups. (b) The higher concentration of free or mobile counter ions in the gel phase also increases the osmotic swelling pressure. Hydrogels do not swell appreciably after pH, it may be due to the presence of electrolyte salts due to ex-osmosis and even the swollen hydrogels shrink dramatically in the presence of salts.<sup>36–38</sup> Hydrogels shrinking results from the loss of hydrophilic–hydrophobic balance of the networks in the presence of electrolyte salts.

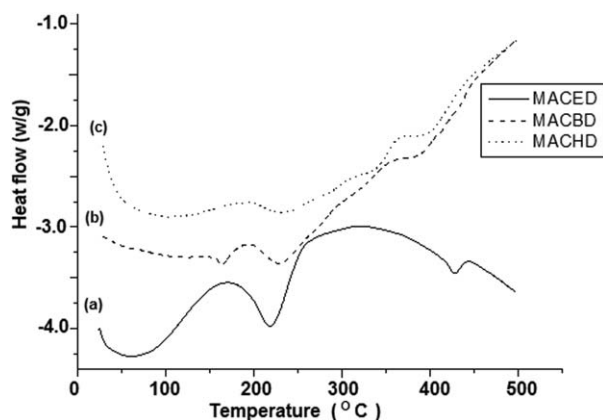
Increase of the chain length of the diol from (ED, BD, and HD) containing two, four, and six carbon, respectively, played a significant influenced swelling behavior of synthesized hydrogels. It is observed that swelling equilibrium changes smartly with the pH of swelling medium. It is obvious that the chain length of carbon increased from ED to HD in a polymeric hydrogels swelling equilibrium decreased with increase of nonpolar alkyl groups (increase of  $-CH_2-$  portion) of the polymer chain. In addition, methyl group affecting pH sensitive nature of poly-

meric hydrogels contributed from the MAA. Based on our previous report on swelling studies reveals that acrylic acid containing citric acid-based hydrogels showed worthy pH-sensitivity. MAA-based hydrogels (MAA-CA) showed good swelling than that of AA-CA-based hydrogels. The presence of  $CH_3$  group reduces surface area of non-polar part in a hydrogels by increasing its free volume and flexibility. Hence, the hydrophilicity increases in the polymer network thus by enhanced swelling equilibrium.

#### Thermal Characterization of Polymeric Hydrogels

Figure 4(a–c) shows the general nature of thermogram of the polymer hydrogels of equimolar composition, *viz.*, MACED, MACBD, and MACHD. The relative thermal stability of different hydrogel was assessed by comparing the weight loss in temperature range ambient to 500°C. It could be seen in Figure 4(a) that MACED hydrogel presents three events of degradation. The first stage ranges between 50 and 160°C corresponding to 8% loss in weight. This may correspond to the loss of adsorbed water. The second stage weight loss starts at 180°C and continue up to 275°C with weight loss 29.96% due to decomposition of different structure of polymeric hydrogels and the third stage degradation occurs in the range of 350–450°C, with

**Figure 4.** TGA curve of (a) MACED, (b) MACBD, and (c) MACHD.**Figure 5.** DTA curve of (a) MACED, (b) MACBD, and (c) MACHD.



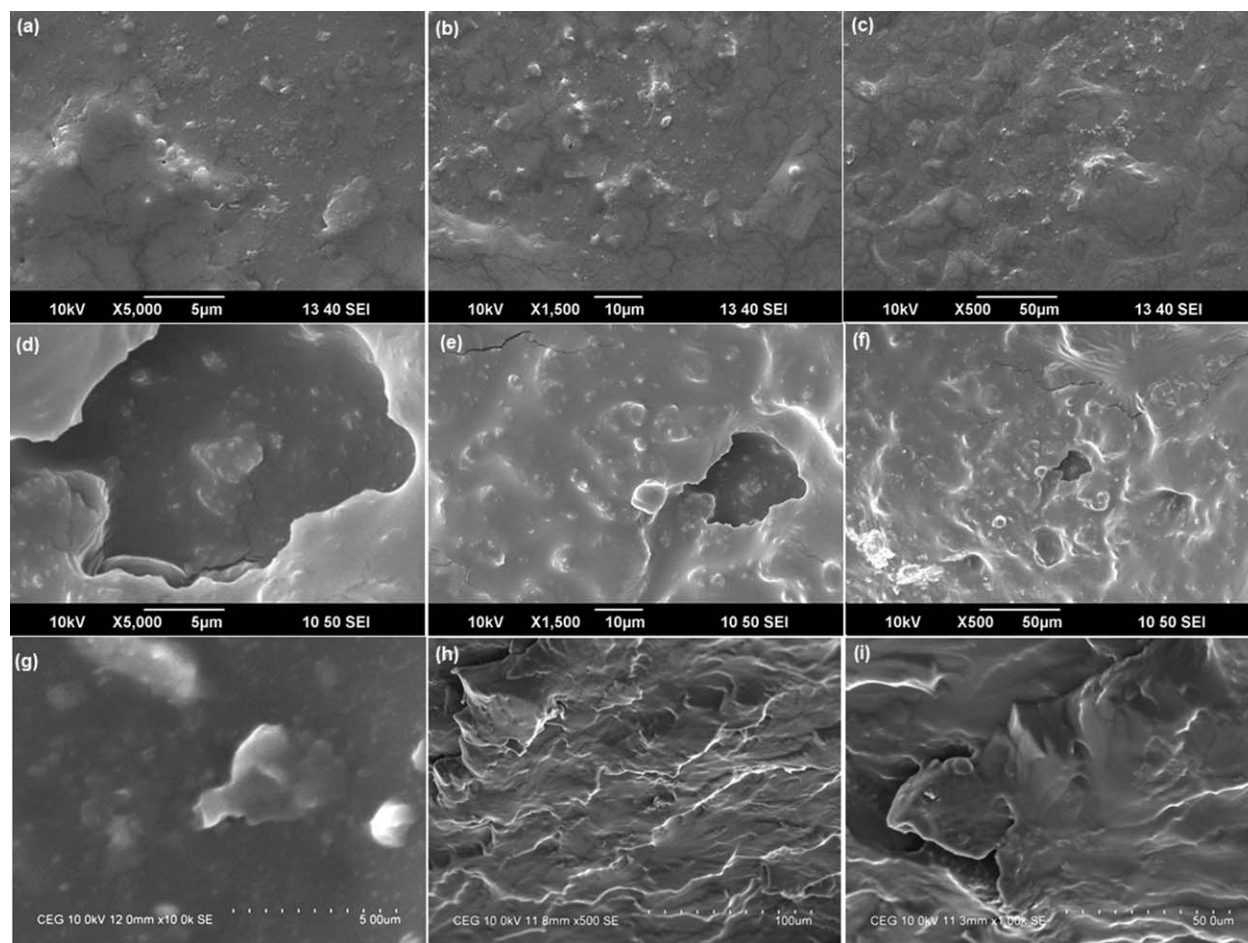
**Figure 6.** DSC thermograms of (a) MACED, (b) MACBD, and (c) MACHD.

weight loss 34.00% might be due to the carbonization of the polymeric materials. TGA curves of MACBD hydrogels shown in Figure 4(b). The mass loss occurs in four stages: the first one refers to the loss of structural water of the hydrogels (153–210°C) with weight loss of 4.404%. The second stage decomposition occurs at 210–296°C with a 25.60% weight loss due to the thermal degradation of the polymeric chains of MACBD and the third stage (290–410°C) with corresponding weight loss

about 39.88% is due to the carbonization of the polymeric materials. Fourth stage decomposition was started at 410°C extended up to 444°C with weight loss about 17.74%. The thermograph of the MACHD [Figure 4(c)] shows that within 100°C weight reduction could be due to moisture loss. First stage decomposition has been observed from 124 to 198°C with 4% weight loss. Second stage decomposition started at 210°C and continues up to 285°C with 20.34% weight loss. Third stage decomposition started at 285°C and continues up to 368°C with 27.74% weight loss. Fourth stage decomposition was started at 368°C extended up to 430°C with weight loss about 36.86%. The DTA curves of MACED, MACBD, and MACHD are depicted in Figure 5(a–c), which supported the TGA results of synthesized hydrogels. Thermal stability order of synthesized hydrogels was found to have MACED > MACBD > MACHD.

#### DSC Thermograms of Polymeric Hydrogels

Figure 6(a–c) showed the DSC thermograms of dried polymeric hydrogels *viz.*, MACED, MACBD, and MACHD, respectively. All scans were obtained for a heating rate of  $10^{\circ}\text{C min}^{-1}$ . All hydrogels were quenched either by dropping the DSC pan containing the samples into the liquid nitrogen and then transferring them into the pre cooled instrument. From Figure 6(a–c), the glass transition temperature of MACED, MACBD, and MACHD was found to have at 27.5, 28.0, and 30°C.



**Figure 7.** Scanning electron microscope picture of (a), (b), (c) MACED (d), (e), (f) MACBD (g), (h), (i) MACHD.

Further, the DSC thermograms of dry hydrogels of MACED, MACBD, and MACHD addressed as endothermic up to 100°C. The MACED sample exhibited a significant feature of endothermic step with an onset temperature of 90°C, conversely, MACBD and MACHD were found to have 135, 145°C as their onset temperature. The extent of linearity of diol group might be the reason behind this jump.<sup>39</sup> Furthermore, the curves in the all hydrogels [Figure 6(a–c)] showed a weak and broad exotherm starting at 190°C and extended up to 250°C which had also been observed by Wilson and Turner<sup>40</sup> as assigned to the crystallization of the hydrogel. The thermal stability of the thermo gravimetric analysis [Figure 6(a–c)] and scanning electron microscopy (SEM) images Figure 7(a–c) followed by the swelling behavior of the polymeric hydrogels MACED, MACBD, and MACHD additional supported the findings in the DSC thermograms.

### Morphologies of Polymeric Hydrogels

SEM technique is useful to reveal hydrogels structure. Figure 7 shows the SEM image of dried MACED, MACBD, and MACHD hydrogels. All the synthesized hydrogels showed uneven-porous and elliptical nature on its surface structure, which permits water and interaction sites of external stimuli with the hydrophilic groups of the polymers. MACED [Figure 7(d–f)] have the fracture and porous structure on their morphology. MACBD [Figure 7(d–f)] hydrogels exhibited a small porous nature on its surfaces, but MACHD hydrogels revealed irregular pores with highly rigid structure and channels within the polymer matrix. It has been recognized in Figure 7(g–i) that MACHD hydrogels have not been permitting fluid to enter into the gaps, leading to substantially drop of the absorption than of MACED and MACBD hydrogels. The equilibrium swelling behavior of synthesized hydrogels at various pH in the following descending order MACHD > MACBD > MACED.

### CONCLUSIONS

In this study, the polymeric pH-responsive citric acid-based hydrogels with varying ED, BD, and HD with methacrylic acid were synthesized. The FTIR spectroscopy confirms the formation and structure of hydrogels. Thermal studies of the hydrogels have been examined by TGA, DTA, and DSC. MACED hydrogel was found to have excellent thermal stability than MACBD and MACHD hydrogels observed from TGA. The stages of decomposition were also being supported by the DTA in addition to TGA analysis for all the synthesized hydrogels. The glass transition temperature of MACED, MACBD, and MACHD was found to have at 27.5, 28.0, and 30.5°C, respectively, from DSC analysis.

Swelling results of hydrogel were also studied at various pH 4.0–10.0 revealed that swelling and swelling equilibrium were higher in neutral and alkaline medium. Results of swelling clearly prove that citric acid has a capacity to tune the swelling behavior. However, increasing chain length of diol drops the swelling behavior from ED to HD. The inverse relationship was noticed, while ascending the diol units of hydrogel in swelling equilibrium. The hydrogels with increasing length of chain length show a noticeable pH sensitivity. Further, the swelling

behaviors of hydrogels well supported by their surface morphology. Moreover, citric acid is low-cost and environment friendly monomer used in the synthesis biocompatible pH responsive hydrogels, Hence, the synthesized biocompatible pH sensitive hydrogels may have a remarkable applications in industrial and biological applications include metal ion removal, cationic dye removal, and controlled release of drugs to pH sensitive parts of human being.

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