

# EFFECT OF CROSSLINKING ON GLASS TRANSITION TEMPERATURE IN SYNTHESIS OF THIOL ACRYLATE-BASED LIQUID CRYSTALLINE ELASTOMERS

Parmida Harirchi, Payam Zahedi\*

Nano-Biopolymers Research Laboratory, School of Chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

## ABSTRACT

Liquid crystal elastomers (LCEs) are a special class of materials including liquid crystalline arrangement and cross-linked polymer network phases. The simultaneous presence of these properties, unique mechanical and optical properties can be happened in LCEs, thereby having wide biological applications. The aim of this work is to synthesize LCEs based on thiol-acrylate Michael addition reaction, to investigate their crosslinking trend and its effect on glass transition temperature ( $T_g$ ) using Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC), respectively. By considering the FTIR results, it has been found that the characteristic peak intensity of thiol groups at wavenumber approximately  $2600\text{ cm}^{-1}$  is decreased due to their contribution in crosslinking process. Interestingly, this decline trend is immense for the sample crosslinked by ultra violet (UV) irradiation. On the other hand, the DSC thermograms of the samples show an increase behaviour in their  $T_g$  by increasing the crosslinker content. The optimum sample with  $T_g$  value approximately  $-7^\circ\text{C}$  is obtained while adjusting the crosslinker content to 75 wt. %. Finally, the obtained results reveal that the variation of crosslinker content is a key role on the polymerization process of LCE samples.

## OBJECTIVES

Liquid crystal elastomers (LCEs) are soft and intelligent materials that are a subset of liquid crystalline polymers (LCPs) with unique characteristics like reversible deformation in response to stimuli. Depending on their properties, LCEs can be used in a variety of fields especially medicine [1-3]. One of the most important parts of these materials is mesogenic units, which are the building blocks of LCEs with small liquid crystal (LC) molecules. LCE phases are formed by different types of mesogens with various features such as calamitic, discotic and bent-shaped. . LCEs consist of mesogenic units [small liquid crystal (LC) molecules], combining the mechanical and elastic properties of common elastomers with the optical functionality as well as molecular ordering of LCs In LCEs, these portions can be directly inserted into the polymer backbone to form either main chain or side group. The main chain of LCEs can orient the mesogens further because it has a direct bond between the mesogenic order and polymeric backbone components [4, 5]. In general, LCEs based on thiol-acrylate polymerization reaction have three components including mesogen (monomer), crosslinker and spacer (an aliphatic group which separates the main chain from crosslinker). In this regard, Saed et al., [6] evaluated glass transition temperature ( $T_g$ ) of LCEs by varying these main parameters of polymerization. They synthesized LCE samples based on a two-step thiol Michael addition polymerization (TAMAP) to assess the  $T_g$  alteration versus different weight ratios of spacer to crosslinker (85:15, 75:25 and 50:50). Their results showed that the  $T_g$  value of the samples was obtain in its maximum amount ( $25^\circ\text{C}$ ) at 50:50 weight ratio. It should be noted that they have not investigated whole weight ratio of spacing to crosslinking agent for detailed investigation.

In this work, thiol acrylate-based LCEs using TAMAP are synthesized and the effect of spacer and crosslinker content on  $T_g$  in the range of (0:100, 15:85, 50:50: 75:25 and 85:15) is investigated. Also, variation of thiol content as a function of ultra violet irradiation time for the optimized sample is evaluated.

## MATERIALS AND METHODS

The di-acrylate mesogen 1,4-Bis-[4-(3-acryloxypropoxy)benzoyloxy]-2-methylbenzene (RM257) was supplied by Wilshire Technologies. The spacer 2,2'-(Ethylenedioxy) diethanethiol (EDDET), The crosslinker Pentaerythritol tetrakis (3-mercaptopropionate) (PETMP), The photoinitiator 2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (HHMP), The Catalyst Dipropylamine (DPA) and The solvent toluene were purchased from sigma Aldrich. To synthesis the LCE samples, in first reaction, a certain amount of RM257 was mixed with toluene to dissolve completely. Then, PETMP and EDDET were added to the mixture. For second reaction, DPA and HHMP were inserted to the polymeric mixture and the UV irradiation was carried out for different times.

Name	Company	Property	Chemical structure
1,4-Bis-[4-(3-acryloyloxypropoxy)benzoyloxy]-2-methylbenzene; RM 257	Wilshire Technologies	Di-Acrylate Mesogen	
Pentaerythritol tetrakis (3-mercaptopropionate); PETMP	Sigma Aldrich	Tetra-Thiol Crosslinker	
2,2'-(Ethylenedioxy) diethanethiol; EDDET	Sigma Aldrich	Di-Thiol Spacer	
2-Hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone; HHMP	Sigma Aldrich	Photoinitiator	
Dipropylamine; DPA	Sigma Aldrich	Catalyst	

A differential scanning calorimetry (DSC, DSC 200 F3 Maia, Netzsch Co., Germany) was utilized to investigate the  $T_g$  alteration. On the other hand, thiol groups consumption by UV irradiation time (0-50 min) was assessed via a Fourier transforms infrared spectroscopy (FTIR, Spectrum Two, PerkinElmer Inc., United States) at room temperature with wavenumbers in a range of  $400\text{-}4,000\text{ cm}^{-1}$  at a resolution of  $4\text{ cm}^{-1}$ .

## RESULTS

Figure 1 shows the DSC thermograms of the LCE samples prepared using different PETMP contents (15-100) as crosslinker to investigate the  $T_g$  variations. As is seen, by increasing the weight percentage of the crosslinker, the  $T_g$  values were increased up to 75 wt.%. Thereafter, a slight decline trend was observed at point of 100 wt. % of PETMP. The reason of this trend change was referred to the absence of spacer (EDDET) in the polymerization chain for the sample including 100 wt.% of the crosslinker which led to decrease the performance of the crosslinker to form a series of binds between the LCE chains.

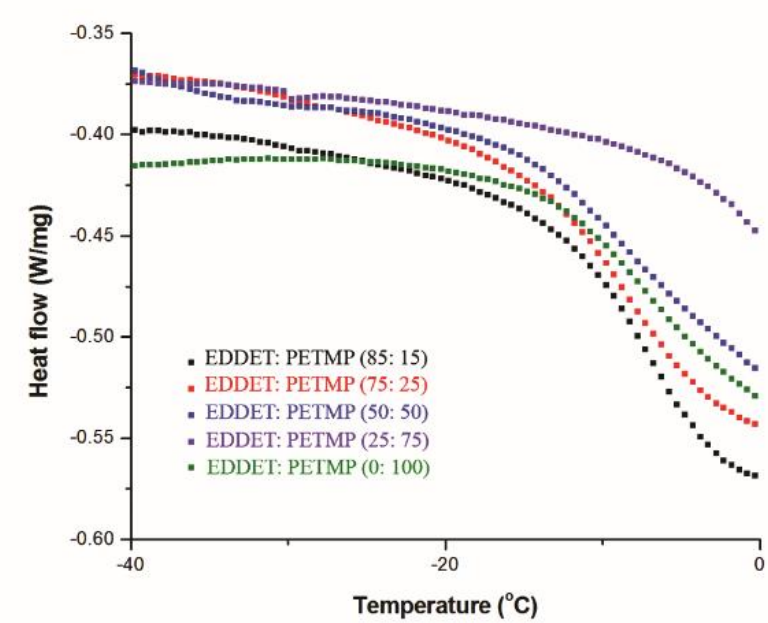


Fig. 1: DSC thermograms of thiol-acrylate based LCEs with different ratios of spacer: crosslinker (EDDET: PETMP)

The FTIR peaks depict in Figure 2 according to the thiol consumption versus UV irradiation time in the sample (EDDET: PETMP 25:75). Evidently, the characteristic peak of thiol groups was appeared at the wavenumber of  $2600\text{ cm}^{-1}$  decreased by increasing the UV crosslinking time. Moreover, the thiol percentage decrease in the sample in the exposure of UV irradiation for 50 min was calculated around 12%. This can be useful for a series of morphology in LCEs which are essential for medical applications [1, 4, 5].

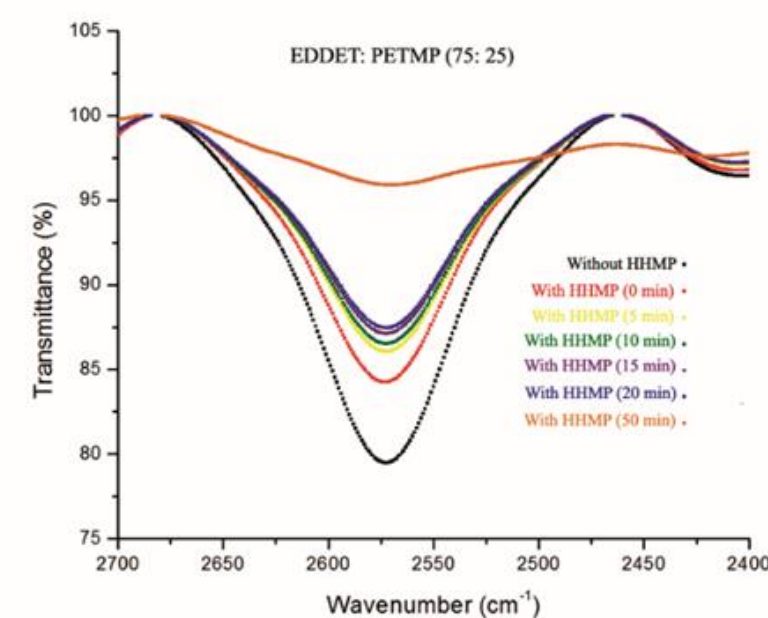


Figure 2: FTIR peaks of thiol-acrylate based LCE samples in the exposure of UV irradiation

## CONCLUSION

Liquid crystal elastomers (LCEs) which are a subset of liquid crystalline polymers (LCPs) remember extraordinary keen materials with numerous abilities for the field of reversible shape change materials because of activations for biomedical applications. It is noteworthy that although LCEs respond to various external stimuli, in fact the appearance of the phase transition phenomenon in these materials is the function of the transition temperature ( $T_{ni}$ ) in which the phase change (anisotropic - isotropic) occurs with reversible deformation.

Herein, the LCEs based on acrylate monomer using TAMAP was successfully synthesized and the their  $T_g$  variations by altering the crosslinking content was studied. The optimum sample was considered with EDDET: PETMP ratio of 25: 75 in which the  $T_g$  value was set about  $-7^\circ\text{C}$ . Afterward, the optimized sample was exposed on the UV irradiation at different times and the results showed that the thiol decrease percentage of 12 after 50 min.

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\* Corresponding Author: phdzahedi@ut.ac.ir



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