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Functionalization and Chemical Modification of 2-Hydroxyethyl Methacrylate with Carboxylic Acid

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Abstract: Free radical polymerization of the resulting monomers methyl methacrylate (MMA), ethyl methacrylate (EMA), methylacrylate (MA) and ethylacrylate (EA) with 2-hydroxyethyl methacrylate (HEMA) (in 1:1 mole ratio) were carried out using azobis(isoboutyronitrile) (AIBN) as initiator at the temperature ranges 60-70 °C. The modification of polymers were carried out by 9-anthracenecarboxylic acid (9-ACA) via the esterification reaction between –OH of poly(HEMA) and –COOH of 9-ACA, in presence of *N,N′*-dicyclohexyl-carbodiimide (DCC), 4-(dimethylamino) pyridine (DMAP) and *N ,N*-dimethyl formamid (DMF). It was found that the molar ratio acid / alcohol/ catalysts= 0.02: 0.02: 0.02 and 0.002, optimal for preparation of the ester. As demonstrated by FT-IR, ^{1}H-NMR and dynamic mechanical thermal analysis (DMTA). The Tg value of methacrylate and acrylate copolymers containing 9-ACA groups was found to increase with incorporation of 9-ACA groups in polymer structures. The presence of 9-ACA groups in the polymer side chains created new polymers with novel modified properties that find some applications in polymer industry. These anthracenic factors could take part in cyclo addition reaction with other factors such as anhydrides and kinons.

Keywords: 2-Hydroxyethyl methacrylate, 9-Anthracenecarboxylic acid, Modified polymers, *N,N′*-dicyclohexyl-carbodiimide.

Introduction

2-Hydroxyethyl methacrylate (HEMA) a hydrophilic, surface active and a high purity dual functionality monomer is widely used in dental adhesive systems and, in its polymeric forms, in numerous biomedical applications[1]. Introducing chemical functionality to polymers provides access to a wide variety of material properties that stem from the functional groups used[2]. Polymers containing carboxylate groups are an interesting research field in polymer and ester chemistry. Attaching the carboxylate groups copolymers chains should lead to important modifications of polymer properties[3]. A number of methods were

established for the esterification of 9-anthracene-carboxylic acid, but most of them require either acidic or basic medium or the application of heat. The esterification of carboxylic acid with HEMA in the presence of DCC and 4-(dimethylamino) pyridine (DMAP) as catalysts was studied[4]. Literature survey reveals that long chain 9-anthracene-carboxylic acids were not esterified with HEMA in the presence of *N,N′*-dicyclohexyl-carbodiimide (DCC). It was observed that (DCC) promotes esterification of alcohols under very mild conditions. All these informations has prompted us to synthesize 9-anthracenecarboxylic esters with an aromatic ring at the side of the ester[5-7]. These anthracenic factors could take part in cyclo addition reaction with other factors such as anhydrides and kinons. The Diels-Alder reaction between anthracene and maleic anhydride to from 9,10-dihydroanthracene-9,10-*α,β*-succinic anhydride was successful and occurred via the Diels-Alder mechanism. Anthracene served as the dien and maleic anhydride was the dienophile.

Experimental

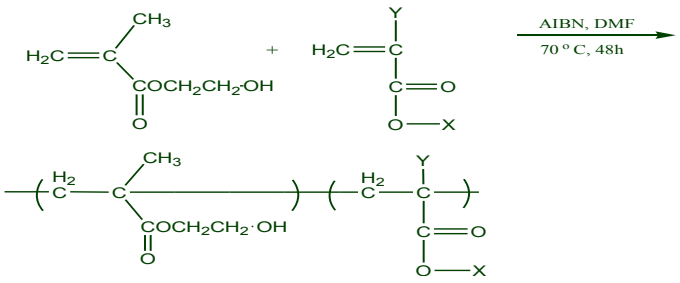
The pure samples 9-anthracenecarboxylic acid (9-ACA), *N,N′*-dicyclohexylcarbodiimide (DCC), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), ethyl methacrylate (EMA), methylacrylate (MA), ethylacrylate (EA) and 4-(dimethylamino) pyridine (DMAP) were obtained from Merck and distilled under reduced pressure to remove inhibitors befor use. Azobis (isoboutyronitrile) (AIBN) was obtained from Fluka and recrystallized from methanol. *N, N*-dimethyl formamide (DMF;Merck) was dried over anhydrous MgSO4 for 2days and distilled under reduced pressure. FT-IR spectra were recorded by use of KBr pellets on a Bruker 4000 spectrophotometer scientific 400IR.^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer at room temperature, using choloroform-d and dimethyl sulfoxide-d_6 as solvent and TMS as internal standard. Dynamic mechanical thermal analysis (DMTA) were characterized by Triton (Tritec 2000 DMN) with rate 10 °C/Min.

Synthesis of the copolymers (I-IV)

Poly(HEMA-co-MMA) (I) or poly(HEMA -co-EMA) (II) or poly(HEMA -co-MA) (III) or poly (HEMA -co-EA) (IV) have been synthesized as general method using 2 g (20 mmol) of MMA or 2.28 g (20 mmol) of EMA or 1.73 g (20 mmol) of MA or 2.00 g (20 mmol) of EA also a mixture of 2.6 g (20 mmol) of HEMA and 0.1 g (0.6 mmol) of AIBN dissolved in 20 ml of DMF. The reaction mixture was heated to 70±1 °C, with constant stirring and under a nitrogen atmosphere. The reaction conditions were maintained for 48 h. Copolymer solution were poured drop wise into a large excess of diethyl ether. The precipitated solid was recovered by filtration, washed with diethyl ether and dried in vacuum at room temperature. The reaction condition are shown in Table 1 and Figure 1.

Table 1. The condition of preparation of copolymers.

Sample	Monomer 1	Monomer 2	Amount of Monomer 1, mmol	Amount of Monomer2 (mmol)	Time, h
I	HEMA	MMA	20	20	48
II	HEMA	EMA	20	20	48
III	HEMA	MA	20	20	48
IV	HEMA	EA	20	20	48



Copolymer	I	II	III	IV
X	CH_3	C_2H_5	CH_3	C_2H_5
Y	CH_3	CH_3	H	H
	MMA	EMA	MA	EA

Figure 1. Copolymerization of HEMA with different monomer 4.

^{1}H-NMR and FT-IR spectra of polymers (I-IV)

Poly(HEMA-co-MMA) (I)

FT-IR (KBr) (cm^{-1}): 3440 (OH), 2953-2996 (aliphatic C-H), 1663 (HEMA C=O), 1732 (MMA C=O), 1663 (CH_2), 1024 –1277 (C-O). ^{1}HNMR ($CDCl_3$) (ppm): δ 0.34-1.3 (s, 6H), 1.6-2.3 (br, 4H), 2.8-3.1(OH), 3.7 (s, 3H), 3.78-4 (br, 2H), 4.1-4.3 (br, 2H).

Poly(HEMA -co-EMA) (II)

FT-IR (KBr) (cm^{-1}): 3493 (OH), 2937 (aliphatic C-H), 1663 (HEMA C=O) , 1730 (EMA C=O), 1023-1275 (C-O). ^{1}HNMR ($CDCl_3$) (ppm): δ 0.7-1.4 (s, 9H), 1.7-2.2 (br, 4H), 2.8-3 (OH), 3.5-3.8 (br, 2H), 3.9-4.2 (br, 2H), (br, 2H).

Poly(HEMA -co-MA) (III)

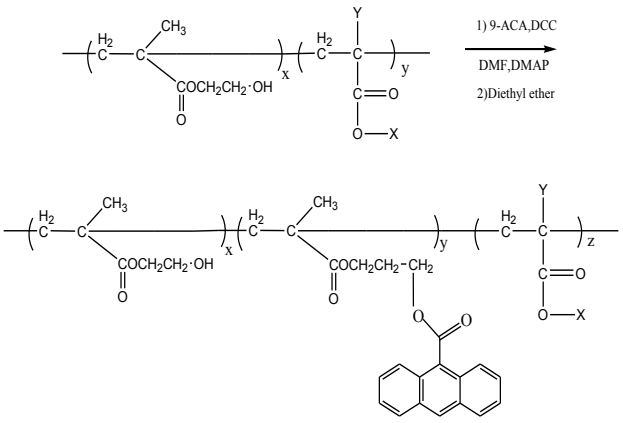
FT-IR (KBr) (cm^{-1}): 3441 (OH), 2928-2952 (aliphatic C-H), 1665 (HEMA C=O) , 1734 (MA C=O), 1025-1222 (C-O). ^{1}HNMR (DMSO) (ppm): δ 0.7-1.2 (s, 3H), 1.2-2.2 (br, 5H), 2.8-3 (OH), 3.3-3.5 (s, 3H), 3.8-4.1 (br, 2H), 4.5-4.7 (br, 2H).

Poly(HEMA -co-EA) (IV)

FT-IR (KBr) (cm^{-1}): 3429 (OH), 2941 (aliphatic C-H), 1668 (HEMA C=O) , 1731 (EA C=O), 1025-1227 (C-O). ^{1}HNMR (DMSO) (ppm): δ 0.7-1.2 (s, 6H), 1.5-2.4 (br, 5H), 2.6-2.8 (OH), 3.4-3.7 (br, 2H), 3.8-4.1(br, 2H), (br, 2H).

Attachment of 9-anthracencarboxylat groups to the side chain of the copolymers

In a two-necked flask 4.45 g (20 mmol) of 9-anthracencarboxylic acid (9-ACA), 4.1 g (20 mmol) of DCC and 0.25 g (2 mmol) DMAP were dissolved in 15 mL of DMF. The flask was cooled until -5 ^{0}C. Then 2.6 g (20 mmol) of copolymers prepared were dissolved in 15 mL of DMF and added to the flask mixture at the mentioned temperature. The reaction mixture was vigorously stirred at -5 ^{0}C for 1 h and returned slowly to room temperature. The mixture was stirred at room temperature about 24 h and filtered for remove of white precipitation of *N,N*-dicyclohexyl urea (DCU). Finally, the obtained polymers were poured drop wise into a large excess of 150 ml cold diethyl ether. The precipitated solid was recovered by filtration, washed with diethyl ether and dried in vacuum at room temperature for 48 h (Figure 2).



Copolymer	I	II	III	IV
X	CH3	C2H5	CH3	C2H5
Y	CH3	CH3	H	H
	MMA	EMA	MA	EA

Figure 2. Reaction of copolymers I-IV with 9-ACA.

^{1}H-NMR and FT-IR spectra of polymers (I_{ACA} -IV_{ACA}) after modified

Poly(HEMA-co-MMA) (I_{ACA})

FT-IR (KBr) (cm^{-1}): 3448 (OH), 3125 (aromatic C-H), 2927 (aliphatic C-H), 1656 (aromatic C=O), 1728 (ester C=O), 1445 (C=C Ar), -1024-1277 (C-O). ^{1}H NMR (DMSO) (ppm): δ 0.4-1.3 (s, 9H), 1.6-2.1 (br, 6H), 2.8-3 (OH), 3.5 (s, 3H), 3.7-4.1 (br, 4H), 4.2-4.5 (br, 4H), 7.5-8.7 (m, 9H).

Poly(HEMA -co-EMA) (II_{ACA})

FT-IR (KBr) (cm^{-1}): 3422 (OH), 3057 (aromatic C-H), 2927 (aliphatic C-H), 1648 (aromatic C=O), 1720 (ester C=O), 1452-1560 (C=C Ar), 1146-1272 (C-O). ^{1}H NMR (DMSO) (ppm): δ 0.7-1.2 (s, 12H), 1.4-2.1 (br, 6H), 2.8-3 (OH), 3.8- 4.1 (br, 4H) , 4.1-4.3 (br, 4H), (br, 2H), 7.5-8.7 (m, 9H).

Poly(HEMA -co-MA) (III_{ACA})

FT-IR (KBr) (cm^{-1}): 3412 (OH), 3055 (aromatic C-H), 2951 (aliphatic C-H), 1667 (ester C=O), 1732 (aromatic C=O), 1446-1562 (Ar C=C), 1025-1197 (C-O). ^{1}H NMR (DMSO) (ppm): δ 0.7-1.1 (br, 6H), 1.6-2.4 (br, 7H), 2.8-3 (OH), 3.5 (s, 3H) , 4.1-4.2 (br, 4H), 4.3-4.7 (br, 4H), 7.5-8.7 (m, 9H).

Poly(HEMA -co-EA) (IV_{ACA})

FT-IR (KBr) (cm^{-1}): 3419 (OH), 3127 (aromatic C-H), 2942 (aliphatic C-H), 1647 (ester C=O) , 1726 (aromatic C=O), 1448-1560 (C=C Ar), 1024-1221 (C-O).
^{1}H NMR (DMSO) (ppm): δ 0.8-1.14 (s, 9H), 1.7-2.4 (br, 7H), 2.7-2.9 (OH), 3.5-3.7(br, 4H), 3.8-4.2 (br, 2H) , 4.2-4.7 (br, 4H), 7.5-8.7 (m, 9H).

Results and Discussion

Monomer of HEMA was copolymerized with methyl methacrylate (MMA), ethyl methacrylate (EMA), methylacrylate (MA) and ethylacrylate (EA) by free radical

polymerization in DMF solution.The presence of the hydroxyl group in HEMA leads to modification of HEMA copolymers for various application[8]. The chemical structure of the related polymers are represented in Figures 1 & 2.

The resulting polymers are soluble in polar aporotic solvents (*e.g.* dimethyl formamide, dimethyl sulphoxide) but insoluble in solvents methanol, ethanol, water and diethyl ether. In the past few decades H-NMR spectroscopic analysis has been established as a power tool for the determination of copolymer compositions because of its simplicity rapidity and sensitivity. The assignment of the resonance peaks in the ^{1}H-NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains[9,10].

The proton resonances of the $–CH_3$ groups in copolymer MMA, EMA, MA and EA at 3.5-3.8 ppm and those the $–CH_2$-OH group in HEMA at 3.8-4.1 ppm are clearly resolved. The copolymers compositions were calculated from the H-NMR spectra data. The molar compositions of HEMA and MMA, EMA, MA and EA in copolymers were calculated from the ratio integrated. Let m_1 be the mole fraction of HEMA and m_2 is that other monomer. HEMA containing 2 methylen protons and MMA, EMA, MA and EA contains 3 methyl protons. The following expression is used to determine composition of copolymer I-IV (Table 2).

Table 2. Molar percentage of copolymer making monomers.

Copolymer	m_1, %	m_2, %
Poly(HEMA-co-MMA)	47	53
Poly(HEMA-co-EMA)	62	38
Poly(HEMA-co-MA)	42	58
Poly(HEMA-co-EA)	48	52

$$\frac{\text{Integrared peak area of 3.8- 4.1 ppm}}{\text{Integrared peak area of 3.5-3.8 ppm}} = \frac{2m_1}{3m_2} = A$$

$$m_1 + m_2 = 1$$

In this work we report the synthesis, characterization and thermal behavior of methacrylic and acrylic copolymers of HEMA without and within 9-ACA groups in the presence of DCC in DMF solution. The resulting modified polymers are soluble in polar aporotic solvents dimethyl sulphoxide but insolvents water and methanol.

In the recent years, studies have been carried out about the attachment of 9-anthracene carboxylic acid to polymers. Also, there are some information about the effects of these groups on the polymers properties. Here is given several types of 9-ACA reaction with different compounds. One of these reaction, is the epoxid ring reaction with 9-ACA, in which produced compound has many applications in the preparation of dielectric thin layers[11,12]. Another reaction of 9-ACA with polymers containing 4-chloromethyl styren, has been investigated. The approach demonstrated in this study facilitates the investigation of the relationship between structure of side-chain groups and polymer properties, providing a general approach for the study of the effect of chemical functionality on material properties of polymers[2].

But here we have succeded in preparing polymers having side chains containing 9-anthracene carboxylate groups the strongly affect the properties of the polymers. There are two ways to introduce functionality to a polymer backbone: polymerization of a prefunctionalized monomer and attachment of functionality to a preformed polymer scaffold via postpolymerization reactions. We chose the second approach, which affords the following three advantages: (a) applicability to a wide variety of functions (while in the first method the modified monomer may unfavorably intervene in the polymerization reaction), (b) ability to create random copolymers with close-to-statistical comonomer distribution by

copolymerization of similar comonomers (of which one is a functionalizable monomer), thus avoiding "blockiness" that may arise from associative processes of like monomers when very different monomers are copolymerized and (c) ability to use the exact same polymer scaffold for the attachment of different functions, which allows isolation and comparison of the functionality contribution to the polymer behavior [2].

Charcterization of copolymers I-IV before and after of modification with 9-anthracenecar-boxylic acid:

Infrared spectra

The asymmetrical and symmetrical streching due to the methyl and methylen groups in copolymers I-IV are abserved 2953 and 2996 cm^{-1}. The band at 1663 cm^{-1} is attributed to the ester carbonyl stretching of HEMA and comonomers and 1732 cm^{-1} is attributed to the ester of comonomers MMA, EMA, MA and EA units. Another band seen at 3440 cm^{-1} is of the hydroxyl group. The bands of 1024 and 1277 cm^{-1} is attributed to the ester C-O stretching of HEMA and comonomers MMA, EMA, MA and EA units. For example IR spectra copolymer (HEMA-co-EMA) shown in figure 3a. The infrared spectra of the modified products show the broad bands characteristic of the no reaction hydroxyl groups at wave number 3422 cm^{-1}. Aromatic =C-H bonds were appeared at 3057 cm^{-1}. The bands at 1720 and 1648 cm^{-1} are attributed respectively to the ester carbonyl stretching of HEMA, comonomers MMA, EMA, MA, EA and aromatic ring. For example IR spectra copolymer (HEMA-co-EMA) shown in Figure 3b.

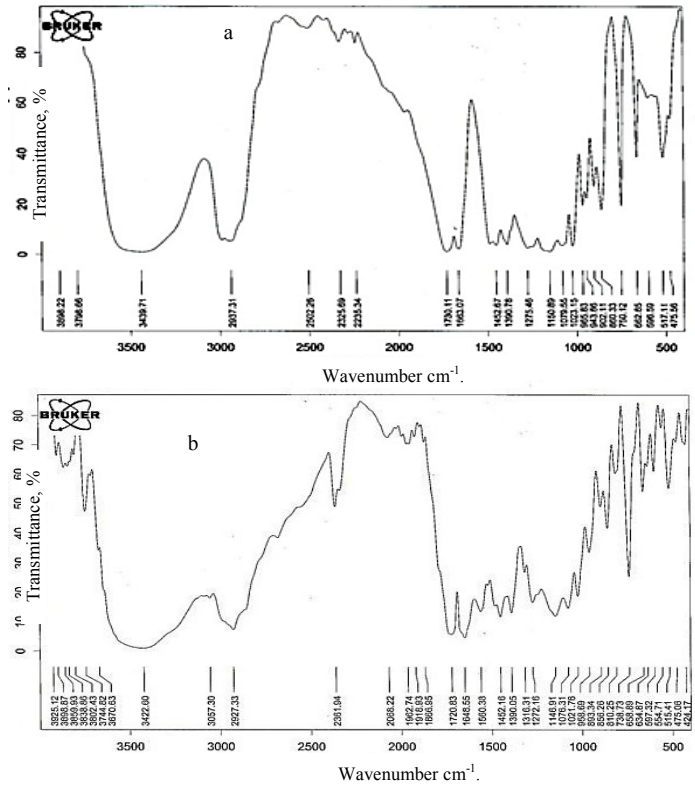


Figure 3. Infrared spectra of poly (HEMA-co-EMA) (a) before reaction with 9-ACA (b) after reaction with 9-ACA.

[1]H-NMR spectra

[1]H- NMR spectra of copolymers I-IV showed two signals at 3.9 and 4.2 ppm due to the splitting of methylene protons in the CH_2-O- group attached to the carbonyl group of the HEMA group. The peak at 1.7-2.2 ppm is due to the methyne proton of hydroxyl group. The resonance signal at 3.5-3.8 ppm was attributed to two methylene protons of $–COOCH_2$- in copolymer EMA ana EA. The resonance signal at 3.7 ppm was attributed to three methylene protons of $–COOCH_3$ in copolymer MMA ana MA. The broad signal at 0.34-1.3 ppm was due to the methylene groups of backbones and other alkyl groups. For examole H-NMR spectra copolymer (HEMA-co-EMA) shown in figure 4a. The [1]H NMR spectra of the pure and modified polymers show the hydroxyl groups (δ=2.64-3.24 ppm), which are well defined in the unmodified polymers decrease after modification. The peaks at 7.5-8.7 ppm are due to the 9-ACA protons. For example H-NMR spectra copolymer (HEMA-co-EMA) shown in Figure 4b.

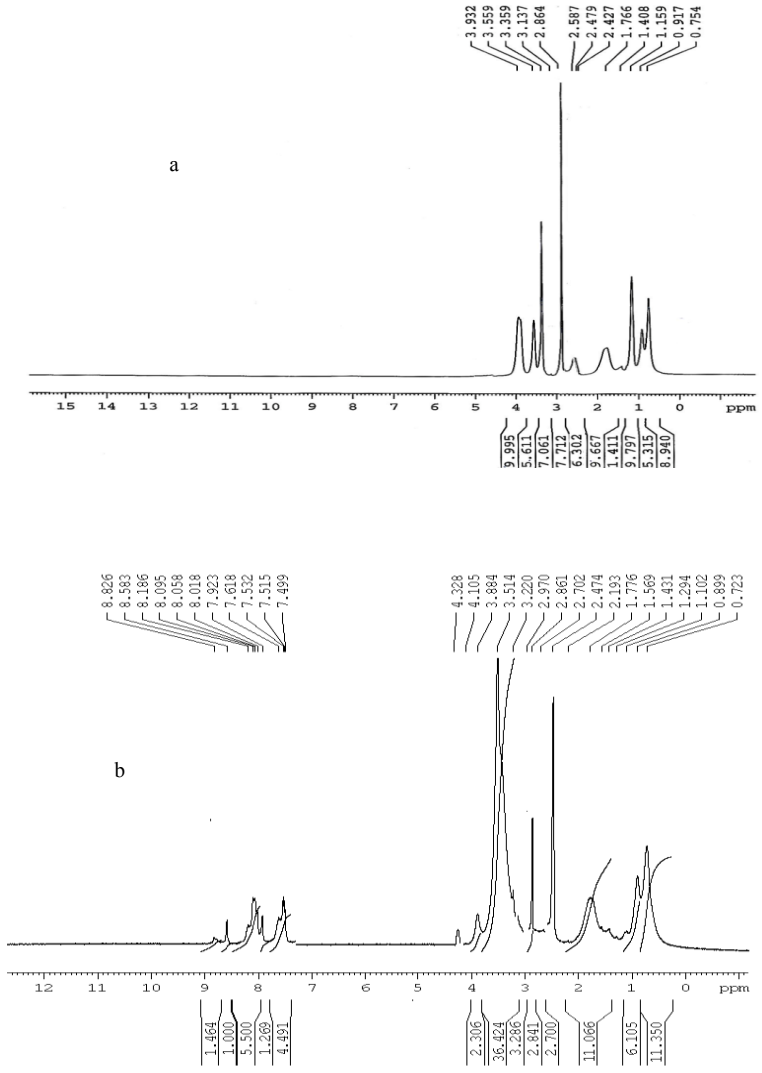


Figure 4. [1]H NMR spectra of poly (HEMA-co-EMA) (a) before reaction with 9-ACA (b) after reaction with 9-ACA.

DMTA curve

The glass transition temperature (Tg) of polymers were determined by Dynamic Mechanical Thermal Analysis (DMTA) Table 3. Glass transition temperature is one of the most essential properties of polymers, dictating important features such as thermomechanical behavior and processing conditions. In the context of microphase separation, for example, reaching the thermodynamically stable, microphase-separated structure requires overcoming the glass transition temperature (Tg) (either by annealing or lowering the Tg by solvent vapor) to allow chain mobility. The DMTA analysis showed that the incorporation of anthracene groups as side chains decrease the free volume of the polymers and therefore, the rigidity and the glass transition temperature (Tg) are increased. DMTA scans show that the presence of bulky 9-ACA groups lead to an increase in the Tg of copolymers.

Table 3. Glass transport temperature of polymers.

Copolymer	Tg, ^{o}C: before modified	Tg, ^{o}C: after modified
Poly(HEMA-co-MMA)	17	40
Poly(HEMA-co-EMA)	17	37
Poly(HEMA-co-MA)	-14	16
Poly(HEMA-co-EA)	-25	14

All the synthesized polymers show a single Tg. The higher Tg value of the copolymer I and II than Tg value of the copolymer III and IV are due to the α-methyl groups, which facilitate chain entanglement, with increasing steric hindered modification of polymers limited. As can be seen by substitution of steric alkyl in acrylat and methacrylate the temperature of polymer Tg is increas by modification via 9-ACA. Because increasing steric hindrance, the possibility of esterization of alcoholic group by acid is being decreased. While the antracenic group is joined to these copolymers, the increase in temperature in acrylat and methacrylate copolymers is evident which is greater in methacrylates. This junction of antracenic group is resulted in decreasing the chains vibration, increasing th temperature of modified Tg polymers. By entering the antracenic groups in the structure of polymers, it is possible to achieve new polymers with fully modified Tg points. These polymers are highly important from view point of new application. DMTA scans show that the presence of bulky 9-anthracene carboxylic acid groups lead to an increasing in the glass transition temperature from 17 °C to 40 °C for polymer I, from 17 °C to 37 ºC for polymer II, from -14 ºC to 16 °C for copolymer III and from -25 °C to 14 ºC for copolymer IV (Figure 5).

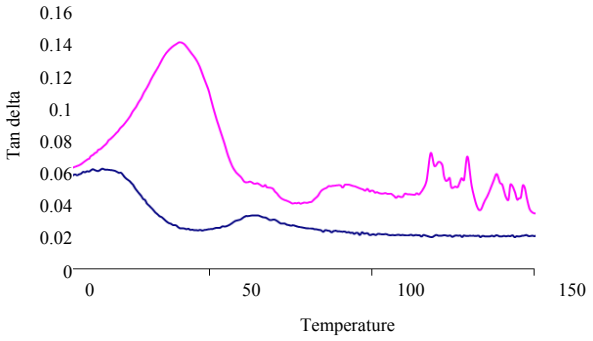


Figure 5. DMTA curves poly (HEMA-co-EMA) (a) before reaction with 9-ACA (b) after reaction with 9-ACA.

Modulus curve

Modulus is one of the mechanical properties that demonstrate material's resistance against deformation under load. The flexural modulus (FM), in particular, measures this behavior under simple beam loading. Variation of modulus with temperature for copolymers of HEMA and modified copolymers with 9-anthracene carboxylic acid has been shown in Figure 5. A considerable decrease in modulus observes for modified copolymers I-IV with respect to before modified copolymers of HEMA. It has been proved that, between the temperature of -50 °C to 350 °C in stable slope of 10 min/ °C, changes of acrylat and methacrylate polymers have been in case of reaction with 9-ACA and making esteric band. Deletion of hydroxyl group removes the possibility of making hydrogenic relation and results in deduction of polymers solidity (Figure 6). The dynamic properties copolymers of HEMA and its modified with 9-anthracene carboxylic acid at various temperature are summarized in Table 4.

Table 4. Modulus change in synthesized polymers.

Copolymers	Modulus change			
	0 °C	25 °C	0 °C	75 °C
Poly-(HEMA-co-MMA)	9.99	9.82	8.61	7.55
Poly-(HEMA-co-MMA) with 9-ACA	9.20	8.32	6.20	6.20
Poly-(HEMA-co-EMA)	7.01	6.35	6.05	5.37
Poly-(HEMA-co-EMA) with 9-ACA	5.65	5.40	3.86	2.58
Poly-(HEMA-co-MA)	6.88	4.93	4.73	4.30
Poly-(HEMA-co-MA) with 9-ACA	6.31	4.66	4.24	4.07
Poly-(HEMA-co-EA)	4.32	4.19	4.08	3.98
Poly-(HEMA-co-EA) with 9-ACA	3.87	3.78	3.66	3.56

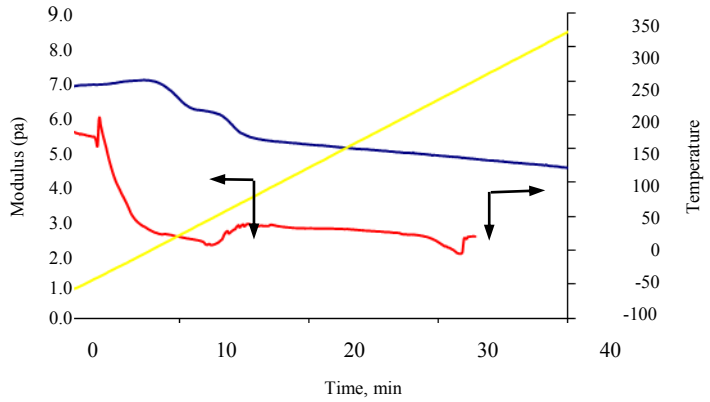


Figure 6. Modulus curves poly (HEMA-co-EMA) (a) before reaction with 9-ACA (b) after reaction with 9-ACA.

Conclusion

The copolymers of HEMA with different methacrylic and acrylic monomers were synthesized by free radical solution polymerization composition calculated by corresponding H-NMR analysis. HEMA copolymers containing hydroxyl side groups have been modified by 9-ACA via the esterification reaction in presence of *N,N'*-dicyclohexylcarbodiimide (DCC). In these cases, parts of the hydroxyl groups are reacted. Such a dramatic reactivity

decrease is likely due to the close proximity of the hydroxyl groups, which leads to a close packing of moieties. Study of the glass transition temperature values of the polymers indicated that glass transition temperature values of all the copolymers I and IV increase with incorporation of 9-ACA groups as side chains.

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