

Characterization and Synthesis of This Comb Type Copolymer with Styrene Using A Macromonomer Containing Polyethylmethacrylate

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Summary: In this study, firstly 7-hydroxy-4-chloromethyl coumarin (CMHC) was synthesized from reaction of ethyl 4-chloroacetate with resorcinol. Then, the poly(ethyl methacrylate) coumarin end grouped having hydroxyl (CEMA) was prepared by ethyl methacrylate with using (CMHC) as initiator by atom transfer radical polymerization (ATRP) method. A macromonomer (CMEMA) was synthesized from reaction of methacryloyl chloride and poly(EMA) ended coumarin having OH group (CEMA). Molecular brush of P(CMEMA-comb-%16St) was synthesized by reaction of macromonomer CMEMA and styrene by free radical polymerization method (SRP). The structures of the prepared macromonomer and molecular brush were characterized by FT-IR and ¹H-NMR techniques. The thermal behavior of P(CMEMA-comb-%St) has been investigated by TGA, and the glass transition temperatures have been measured on DSC. The average molecular weights and polydispersity were determined by GPC. The dielectric behavior of P(CMEMA-comb-%16St) was investigated as a function of temperature and frequency. The intrinsic viscosity [η] of P(CMEMA-comb-%16St) was determined.

Keywords: Macromonomer, Comb Copolymers, Dielectric properties, Intrinsic Viscosity, Polymer.

Introduction

Molecular comb or brushes are a characteristic type of graft copolymers formed by the multi polymer chains grafted in order to form linear polymers. Generally they consist of groups such as the main chain backbone and side chain. If the main chain is longer considerably than the side chains, the shape of the molecule will be cylinder and the side chains wraps the molecule as they are connected to the center. Reversely, the molecular brushes based on backbones on pending of the lengths of the side chains comprehensively internalize spherical, compact dimensions that appear like star polymers [1, 2]. These types of polymers are not only the homo-polymers but they can also be block copolymers, graft copolymers and polymers with different compositions including molecular brushes [3]. These polymers may be grafted from the surface [4]. And also be used as gels cross-bound physically and chemically. Stimuli such as temperature, pH, ionic power, light and magnetic field [1-5] may be used to influence the polymer features. Generally, the reversible solubility controlled and polymeric micelle and vesicle shaped molecules become together themselves and consist of the polymers that are sensible to the stimuli [1]. And these polymers are sensitive to changes to build a new structure as well. These polymers with unique features are used in many fields such as in medicine systems, for DNA sequencing in tissue and system engineering, in carbon nanotubes, in modification of the environmentally responsible smart materials,

thermoplastic elastomers [6] optical and chemical sensors [7, 8]. Additionally, it has attracted great interest in developing the original material specifications like supersoft elastomers [9]. Due to their branched structure they generally have lower melt viscosities that constitute an advantage for processing [10]. The radical polymerization living controlled (CRP), synthesis of polymer with easy molecular weight control, and synthesis of polymers with narrow molecular weight distribution have constituted multipronged pathways in synthesizing the molecular brushes polymerization techniques namely. Atom transfer radical polymerization (ATRP), reversible additional fragmentation chain transfer polymerization (RAFT) and stable free radical polymerization (SFRP) have been successfully used in synthesis of such polymers [1-11]. The feature that makes the molecular brushes unique and important is the molecule separation which is the resolute state as result of the intensively grafted chains steric repulsion [1]. In general, three methods has been showed in synthesis of the molecular brushes: "Grafting through" the polymerization of macromonomers [12] "Grafting to" connection of the side chains on the backbone and "Grafting from" grafting side chains from backbone [6-13]. Copolymers brush-typed are the materials that involve a linear backbone with a high grafting density of side chains [14]. The determinants of total molar mass are the backbone length, grafting density and side chain lengths. And these determinants affect

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the properties of materials structured with such macromolecules [14, 15].

In current our study; we report the synthesis of the poly(ethyl methacrylate) coumarin end grouped having hydroxyl (CEMA) by ATRP method. The macromonomer (CMEMA) was prepared from reaction of methacryloyl chloride and CEMA synthesized. The comb copolymer of P(CMEMA-comb-%16St) was prepared from macromonomer (CMEMA) with styrene by free radical polymerization method. The characterization of the obtained macromonomer and comb copolymer were carried out by FT-IR, ¹H-NMR, DSC, TGA, GPC and impedance analysis.

Experimental

Materials

Styrene (St) and ethyl methacrylate (EMA) (Aldrich) were distilled under vacuum before use. Cuprous(I) bromide CuBr, 2,2'-bipyridine (bpy), 2,2'-azobisisobutyronitrile (AIBN), resorcinol, ethyl 4-chloroacetoacetate, methacryloyl chloride, triethyl amine (TEA), anhydrous MgSO₄, 1,4-dioxane, tetrahydrofuran (THF), dichloromethane, ethanol, n-hexane, acetone were used without further purification.

The infrared spectra for characterization of macromonomer and comb copolymer have been recorded using Perkin-Elmer Spectrum One FT-IR spectrometer. The ¹H-NMR spectra have been recorded using 400 MHz Avance III Bruker spectrometer. The CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard have been used. The average molecular weights and polydispersity index were measured by using Agilent 1100 gel permeation chromatography (GPC) with a Waters Styragel column, RI (refractive index) detector, and the column was calibrated by polystyrene. The differential scanning calorimetric (DSC) measurement was carried out on a Shimadzu DSC-50 by a heating rate 20 °C/min under N₂ flow. The thermogravimetric analysis (TGA) measurement was performed on a Shimadzu TGA-50 with heating rate 10 °C/min under N₂ flow. The dielectric measurement was carried out at 298 K and 423 K with a Quad Tech 7600 precision LRC Meter impedance analyzer over the frequency rate 100 Hz – 2 kHz. The viscosity measurements were carried out by Ubbelohde viscosimeter at 25 °C in presence of 1,4-dioxane solvent.

Synthesis of Macromonomer and Comb Copolymer Synthesis of 7-Hydroxy - 4 -Chloromethyl Coumarin [CMHC]

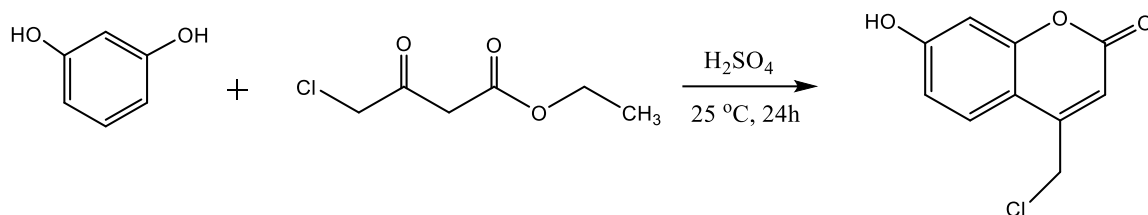
Resorcinol (0.06 mol), ethyl 4-chloroacetoacetate (0.06 mol) and (20 ml) H₂SO₄ have been placed in a 250 ml three necked flask and mixed at the room temperature for 24 h. The obtained product has been precipitated in the water (100 ml) at room temperature and crystalized within the mixture of acetone-alcohol with a rate of 2:1 [16, 17]. The synthesis method is shown in Scheme-1.

Synthesis of 7-Hydroxy- 4-Methyl Coumarin end Grouped P(EMA) [CEMA]

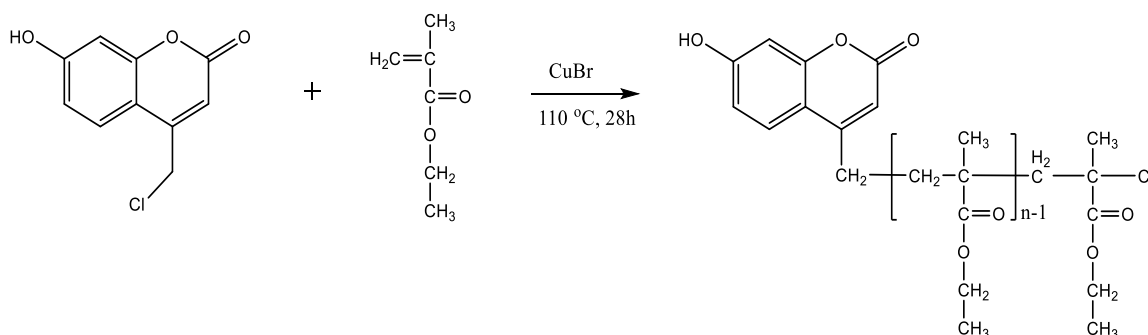
In a polymerization tube, in which the ATRP method had been used as macroinitiator: CuBr: 2, 2'-bipyridine: monomer: have been placed with regard to the rates of 1:1:2:100 (mol) respectively. The 2, 2'-bipyridine (1.052x10⁻³ mol) as ligand and CuBr (5.26x10⁻⁴ mol) as catalyzer have been placed into a polymerization tube. The mixture has been passed from argon gas, then 7-hydroxy -4- chloromethyl coumarin (CMHC) (5.26x10⁻⁴ mol) have been added as macroinitiator. The ethyl methacrylate (EMA) monomer (0.0526 mol) have been added into the mixture. The argon gas has been passed through the tube for 10 minute and then the mouth of the tube has been closed. It has been placed in an oil bath at 110 °C. The polymerization process has been lasted for 28h, the obtained product has been solved in dichloromethane and precipitated in cold hexane. The synthesis method is shown in Scheme-2.

Preparation of Macromonomer from Synthesize with Methacryloyl Chloride of CEMA [CMEMA]

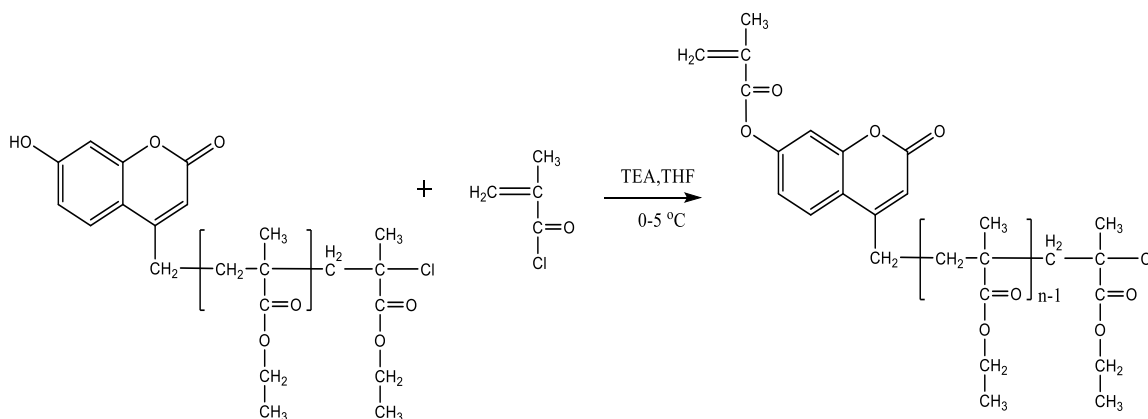
Methacryloyl chloride (0.02 mol), and triethyl amine (TEA) (0.02 mol) have been placed to a three-necked flask and mixed by a magnetic mixer in the temperature interval of 0-5 °C. The 7-hydroxy-4-methyl coumarin end grouped polyethyl methacrylate (0.02 mol) have been dissolved in tetrahydrofuran (THF) (20 ml) and added to the reaction flask for 30 minutes by dropping funnel, mixed for 8 h at the room temperature. The triethylammonium chloride salt was removed by filtration. THF was evaporated under vacuum from the solution. After the produce was washed with NaHCO₃ solution and dried in MgSO₄. The resulting product has been dried at 40 °C in vacuum oven for 24 h. The synthesis method is shown in scheme-3.



Scheme-1: Synthesis method of CMHC.



Scheme-2: Synthesis method of coumarin end grouped P(EMA).



Scheme-3: Synthesis method of CMEMA.

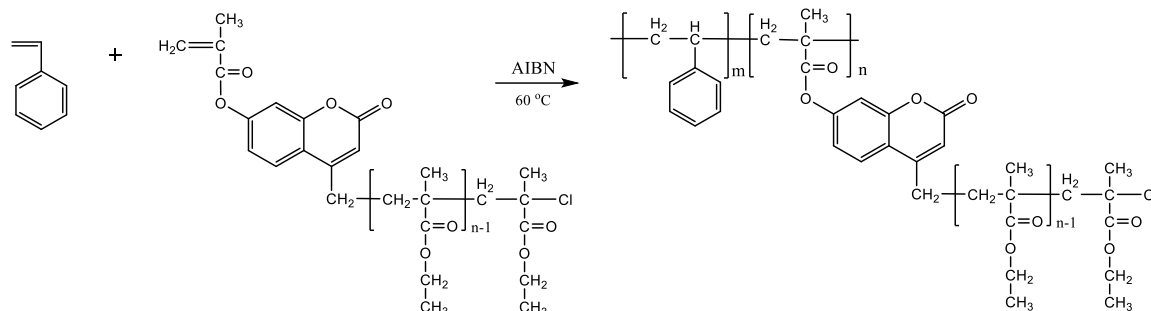
Comb Copolymerization of Styrene with Macromonomer (CMEMA) [P(CMEMA)-comb-St] by "Grafting Through"

To a polymerization tube was placed CMEMA and styrene monomer solution in 1,4-dioxane (2 ml as solvent) (0.5 g CMEMA- 0.2 g styrene), in presence of AIBN as initiator. The prepared mixture has been polymerized at 60 °C in oil bath for 48 h by free radical polymerization method. The synthesized copolymer has been precipitated within n-hexane. The product has been dried for 24 h at 40 °C under vacuum. The synthesis method is shown in scheme 4.

Results and Discussion

Synthesis and Characterization

In this study, at the first stage, 7-hydroxy-4-chloromethyl coumarin (CMHC) initiator that prepared in our laboratory has been synthesized [17]. In (CMHC)'s FT-IR spectrum, phenolic OH strain 3270 cm^{-1} , aromatic and aliphatic C-H strains at 3085-2850 cm^{-1} , respectively, OC=O (the peak belongs to carbonyl group on coumarin ring) at 1695 cm^{-1} , aromatic C=C double bond strain at 1615 cm^{-1} , aliphatic C-H bending vibration at 1440-1315 cm^{-1} are the most characteristic peaks for the structure. In $^1\text{H-NMR}$ spectra, OH at 10.45 ppm, aromatic ring protons at 7.70-6.45 ppm, $-\text{CH}_2\text{Cl}$ protons at 4.90 ppm are the most important signals, which characterize the structure.



Scheme-4: Synthesis method of P(CMEMA-comb-St).

At the second stage, 7-hydroxy-4-chloromethyl coumarin (CMHC) used as initiator for the ATRP method has been interacted with ethyl methacrylate monomer, and 7-hydroxy-4-methyl coumarin end grouped polyethyl methacrylate (CEMA) was produced. In this work, the CEMA was used as macroinitiator for ATRP to prepare comb copolymer. The FT-IR spectrum showed new bands at 1730 cm^{-1} ($-\text{OC}=\text{O}$ ester carbonyl) in the methacrylate structure, at 1607 cm^{-1} (aromatic $\text{C}=\text{C}$ strain). In the $^1\text{H-NMR}$ spectra, aromatic ring protons at 7.4 ppm, at 8.3 ppm $-\text{OH}$, and $-\text{OCH}_2$ protons at 4.1 ppm are important signals characterizing produced the structure. At the third stage, the (CMEMA) macromonomer has been prepared from reaction of 7-hydroxy-4-methyl coumarin end grouped polyethyl methacrylate (CEMA) with excessive methacryloyl chloride. The obtained product was recrystallized within THF. The FT-IR and $^1\text{H-NMR}$ spectra for the obtained CMEMA are given in (Supp. Inf. Fig. S1 and S2).

In the FT-IR spectrum showed important bands at $3080\text{-}2850\text{ cm}^{-1}$ aromatic and aliphatic C-H strain, at 1730 cm^{-1} , $-\text{OC}=\text{O}$ ester carbonyl, at 1610 cm^{-1} , $\text{C}=\text{C}$ double bond strain belonging to aromatic ring, and the small signal at 3430 cm^{-1} characterizes the overtone band belonging to carbonyl group. $^1\text{H-NMR}$ spectrum confirmed structure of CMEMA with important signals at 7.87-6.50 ppm aromatic ring protons, at 4.00 ppm, $-\text{OCH}_2$, at 4.1 ppm $-\text{OCH}_2$ protons exist on ethyl methacrylate unit on the chain end, the protons belonging to H on the $-\text{CH}_2$ at 1.8-2.1 ppm, and $-\text{CH}_3$ protons on the side group at 0.8-1.4 ppm. Moreover, the coumarin group that occurs end part of macromonomer was characterized by the weak signals between 5.90-4.40 ppm in the $^1\text{H-NMR}$ spectra. The OH peak also disappearance on $^1\text{H-NMR}$ of CMHC at 10.45 ppm, depicts the formation of methacrylate end grouped CMEMA.

The P(CMEMA-comb-St) has been synthesized from CMEMA macromonomer and styrene by using the

free radical polymerization method. The IR and $^1\text{H-NMR}$ spectra of comb copolymer is showed in (Supp. Inf. Fig S3 and S4)

The aromatic and aliphatic C-H strain at $3060\text{-}2985\text{ cm}^{-1}$, ester $-\text{OC}=\text{O}$ in copolymer composition at 1730 cm^{-1} characterize the strain vibration of the ester carbonyl; the $\text{C}=\text{C}$ bond on the aromatic ring strain at 1602 cm^{-1} characterizes C-O asymmetric stretching vibration at 1147 cm^{-1} . In the $^1\text{H-NMR}$ spectra of P(CMEMA-comb-St) is important peaks characterizing $-\text{OCH}_2$ protons at 3.90 ppm signal, the aromatic ring protons at 7.2 and 6.5 ppm and the $-\text{CH}_2-$ protons belonging to the ester oxygen on the main chain at 0.8-2.1 ppm and $-\text{CH}_3$ protons on the side group.

The comb copolymer composition has been calculated from the $^1\text{H-NMR}$ spectra. For this aim, the integral height of the protons at (7.2-6.5 ppm) in the aromatic region belonging to the styrene moieties and the integral height of the $-\text{OCH}_2$ protons of the CMEMA units at 3.90 ppm were compared, and the compositions of %Styrene and %CMEMA (by mol) in the copolymer were calculated by the equation given below.

$$C = \frac{\text{Integral height of the aromatic protons}}{\text{Integral height of } -\text{OCH}_2 \text{ in EMA units}} = \frac{5m_1}{2m_2}$$

$$m_1 + m_2 = 1$$

m_1 = CMEMA mol fraction of the macromonomer, m_2 = mol fraction of the styrene

According to the equation above, the m_1 and m_2 values have been determined. The composition of the P(CMEMA-comb-St) has been calculated as %84 CMEMA and %16 styrene. The average molecular weights of the P(CMEMA-comb-%16St) and polydispersity index have been determined by Gel Permeation Chromatography indicated in (Supp. Inf. Fig.S5) and (Table-1), respectively.

Table-1: GPC results of P(CMEMA-comb-%16St).

Polymer	M _n	M _w	M _z	M _v	HI (M _w /M _n)
P(CMEMA-comb-%16St)	6900	11500	17600	11500	1.68

The number average molecular weight (M_n) and polydispersity (HI) values of comb copolymer were found as (M_n=6900g/mol), (HI=1.68). The polydispersity of P(CMEMA-comb-%16St) was found to be close to each other by depending on type of the polymer chain. This shows that the contributed of chain breaks and transfer as well as the termination reactions throughout copolymerization can be negligible till higher polymerization conversion [18-24].

Thermal Analysis of Comb Copolymers

The glass transition temperature of the P(CMEMA-comb-%16St) and macromonomer have been estimated from DSC thermogram (supp. Inf. Fig. S6 and S7). For this aim, about 5 mg of polymer sample has been heated to 200 °C with a heating rate of 20 °C/min under argon flow and DSC curve has been recorded. Both DSC curve of comb copolymer and macromonomer are showed the single glass transition temperature that observed to show homogeneous phase distribution of the macromonomer and comb copolymer composition are understood from a single T_g value. Moreover, the CMEMA glass transition temperature T_g has been determined as 122 °C by DSC. The T_g of the comb copolymer containing styrene has been estimated as 107 °C. The T_g value with the introduction of styrene unit to copolymer system has been importantly decreased. According to this result, the styrene units by penetrating into the structure of the polymer have increased the chain movements and free volumes and T_g has decreased [19-24].

The thermal decomposition of comb copolymer has been used TGA-50 technique. For this purpose, about 5 mg sample has been made by heating up to 500 °C under N₂ flow at 10 °C /min heating rate. The TGA curve recorded has been given in (Supp. Inf. Fig. S8) and it showed decomposition curve with single stage. The initial decomposition temperature, final decomposition temperature and the temperatures up to %50 weight loss are found as 213 °C, 411 °C and 325 °C, respectively.

Dielectrical Behaviors

The change at the polymers dielectric specifications are a measure for electronic, ionic and molecular polarizability. These features are being associated with the physical and chemical structure of

the polymers. For this purpose, the dielectric measurements of P(CMEMA-comb-%16St) have been investigated by using the LCR Meter Impedance Analyzer device. For this aim, 0.1 g P(CMEMA-comb-%16St) has been powdered under pressure of 4 tons and transformed into disk. Its thickness has been measured and the disk surfaces were coated by silver paint.

The capacitance measurements have been recorded at different frequencies (100Hz to 2 kHz) and temperatures (298 to 423K) by impedance analyzer. Dielectric constants have been quantified by the help of the formula below [20, 21].

$$\epsilon = C \cdot \frac{d}{\epsilon_0 \cdot A} \quad (1)$$

C=capacitance value, d=thickness, A=sphere of influence, ε₀= permeability of the space, ε'=dielectric constant.

Dielectric loss factor in the polymer has been calculated by the ε''=Df.ε' formula. Dielectric constant determined at room temperature and at 1 kHz for the P(CMEMA- comb-%16St) was found as (ε'= 3.21). The dielectric properties were observed that change by the frequency in (Fig. 1 and 2). Dielectric constants (ε') and dielectric loss factor (ε'') of the comb copolymer have been observed to decrease with increase in frequency [22, 23]. It has been observed that the capacitance values of the comb copolymer has increased as the frequency increases, then it has started to decrease after a maximum exceeded and has remained stable at high frequencies. It may be said that this is probably an indicator of polarizability of the interval surfaces [25].

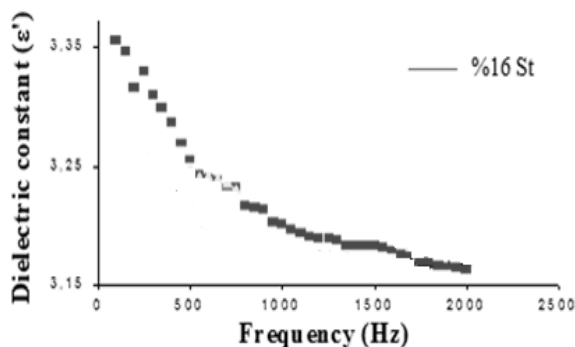


Fig. 1: The graph of dielectric constant versus the frequency for P(CMEMA-comb-%16St).

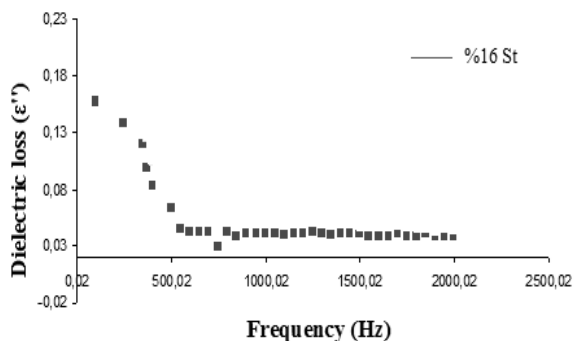


Fig. 2 The graph of dielectric loss factor versus the frequency for P(CMEMA-comb-%16St).

As the electric field has been applied moving loads will occur on the polymer surface that is the surface loads. When the electric field applied, these loads cause superficial polarization by cumulating on the dielectric surface [22]. And this leads dielectric constant to decreases as the frequency increases. The dielectric constants of comb copolymer have increased with increasing temperature (Fig. 3). As the polymers are stagnant and immobile under the glass transition temperature, when an electric field applied to the polymer, polarization increases and polymers chain movements will increase as the volume increases at the glass transition temperature, and spaces will occur. This will lead to dielectric constant to increase by the temperature [24].

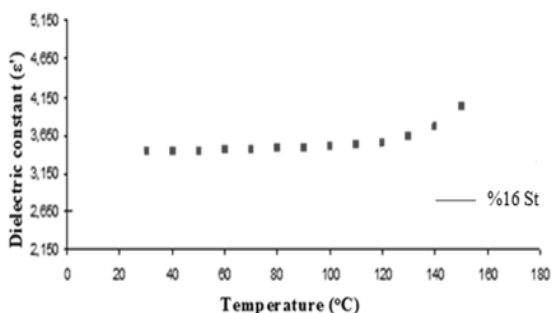


Fig. 3: The graph of dielectric constant versus temperature for P(CMEMA-comb-%16St).

Viscosity Measurement

The viscosity measurement of comb copolymer was determined by Ubbelohde viscosimetry at 25°C and 1,4-dioxane used as solvent. In order to determine specific viscosity (η_{sp}) value was used Huggins relation.

$$\eta_{sp} = [\eta] \cdot C + k' \cdot [\eta]^2 \cdot C^2 \quad (2)$$

$$\eta_{sp}/C = [\eta] + k' \cdot [\eta]^2 \cdot C \quad (3)$$

where C = concentration, $[\eta]$ = it is intrinsic viscosity obtained by extrapolating a plot of η_{sp}/C against concentration C and it is characteristic parameter for a polymer.

According to Huggins relation, the graph has been plotted between specific viscosity coefficients (η_{sp}/C) versus concentration (C). The plots were linear to obtain a the Huggins constant (k') from the slope and by extrapolating linear plots to zero concentration the intrinsic viscosity $[\eta]$ were found from intercept of the intrinsic viscosity axes (Fig. 4).

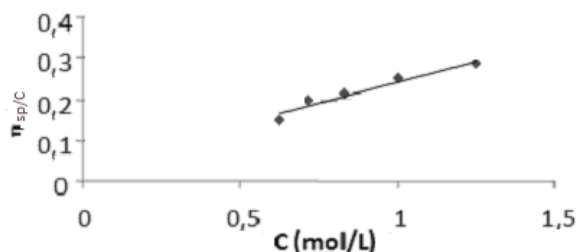


Fig. 4 The P(CMEMA-comb-%16St) comb polymer $C \rightarrow \eta_{sp}/C$ graph.

To determine the thermodynamic properties of polymers are very important interactions soluble-solvent. The viscosity in determining these interaction is a decisive factor for practical and theoretical purposes. The comb polymers, for carry on a large scale branched units in the polymer chain, affected substantially physical properties such as viscosity and solubility. Generally, due to their branched structure have a lower melt viscosity to process [10]. Therefore, the intrinsic viscosity of P(CMEMA-comb-%16St) was calculated from Huggins relation. For P(CMEMA-comb-%16St) $[\eta]$ value was found as $[\eta] = 0.038$ dl/g. Decreasing the viscosity value, it said that have low interaction with solvent of comb copolymer [26, 27].

Conclusion

The P(CMEMA-comb-%16St) copolymer system was prepared in case of four steps. The FT-IR and $^1\text{H-NMR}$ spectroscopic techniques were used for characterization of comb copolymers. Thermal behavior and the glass transition temperatures were determined by TGA and DSC, respectively. The

average molecular weight and polydispersity index were measured by GPC. The number average molecular weight (M_n) for P(CMEMA-comb-%16St) was measured as ($M_n = 6900 \text{ g.mol}^{-1}$). The polydispersity index was found as (HI= 1.68). Dielectric constant and dielectric loss factor of the comb copolymer were decreased with frequency increasing and increased with temperature increased. The intrinsic viscosity value of P(CMEPA-comb-%16St) was found as $[\eta] = 0.038 \text{ dl/g}$.

Supporting Information

Spectra of FT-IR and $^1\text{H-NMR}$ of macromonomer and comb copolymer, the curves of average molecular weights, thermograms of TGA and DSC.

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