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Evaluation of the (Allyl alcohol 1,2-butoxylate-*block*-etoxylate)-*b*-PMMA Copolymers Composition by the Dielectric Measurements

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Redox initiated free-radical polymerization of methyl methacrylate (MMA) with allyl alcohol 1,2-butoxylate-*block*-etoxylate (AABE) was carried out to yield AABE-*b*-PMMA copolymers at elevated temperatures. The composition of the copolymers depending on the polymerization temperature was qualitatively estimated by the dielectric measurements. It has been seen that AABE segment quantity decreased and PMMA segment quantity increased with increasing the polymerization temperature. The dielectric constant and the dissipation factor of the copolymers were investigated as a function of frequency and temperature. The dielectric constant and the dissipation factor were found to be strongly affected by the polymerization temperature. The highest dielectric constant in all studied temperatures and frequencies was obtained in the case of the copolymer which was prepared at 313 K. The dipolar C-O and OH groups of the AABE segment have the primary effect on the dielectric constant. The copolymer which was prepared at 323 K, showed the highest dissipation factor near the relaxation temperature of PMMA.

Keywords: allyl alcohol 1,2-butoxylate-*block*-etoxylate; dielectric constant; dissipation factor; dielectric relaxation; poly(methyl methacrylate); redox polymerization

1 Introduction

Polar structural polymers have attracted more attention, especially in the electric and electronic device industries. The dielectric properties of the copolymer materials entirely depend on the dipolar structure of the monomer units, their distribution in the main chain and the percentage in the composition. The dielectric properties are strongly affected by the medium temperature and the frequency. The effect of the medium temperature on the dielectric properties arises in two ways. First, the ability of the molecular movements becomes easier with increasing the temperature and thus the polar groups easily orient in the direction of the external field. This effect was easily observed in the glass transition region. Second, the increasing thermal movements of the dipole groups prevent their orientation. Both effects depend on the equilibrium temperature and the number of the polar groups per unit volume. Besides, the amount of oriented dipole moment also depends on the external field frequency. This dependency comes from the dependence of the relaxation time of the dipole groups on the frequency and the temperature. Therefore, the investigation of the dielectric properties of polymers related to the frequency and the temperature is one of the experimental procedures to obtain information about the dipolar structure (1, 2). The dielectric measurements of polymers are performed from the static state to the microwave frequency range (2–15).

Redox polymerizations, initiated by free radicals formed via oxidation-reduction reactions, are normally characterized by very short induction periods, high polymer yield in a short time, and the possibility of performing polymerization at room temperature (16). Many redox pairs have been used as initiators in aqueous polymerization, their water solubility being the essential feature. Ceric salts show a high reactivity in aqueous media and have been used either alone or in combination with reducing agents as initiators of vinyl polymerization. The ceric ion proceeds via single-electron transfer with the formation of free radicals from the reducing agent (17). Cerium(IV) ion has been used for the oxidation of many organic compounds in the form of cerium(IV) ammonium nitrate, cerium(IV) ammonium sulfate, cerium(IV) sulfate and ceric perchlorate and the mechanism of such reactions has been well established (18). The oxidation of alcohols by Ce(IV) is believed to proceed by disproportionation of coordination complexes.

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Evidence of complex formation has been obtained in Ce(IV) oxidations of many compounds in perchloric and nitric acid media (17).

In free radical polymerization of allylic monomers, macroradicals are generated similar to the free radical polymerization of vinyl monomers. However, terminations of kinetic chain proceed by degradative chain transfer to monomer which leads to self-inhibition of the polymerization (19). The most characteristic feature of polymerization of monoallyl monomers is of the significance of facile monomer chain transfer, which competes with normal propagation, yielding polymers of medium-molecular-weight or oligomers and produces resonance-stabilized allyl radical, causing the allyl monomers to retard polymerization (20).

The dielectric properties of the copolymers will vary depending on the copolymer composition. This study has been proposed to estimate the AABE-*b*-PMMA copolymers composition by the dielectric measurements of the copolymers which were prepared at elevated temperatures.

2 Experimental

2.1 Materials

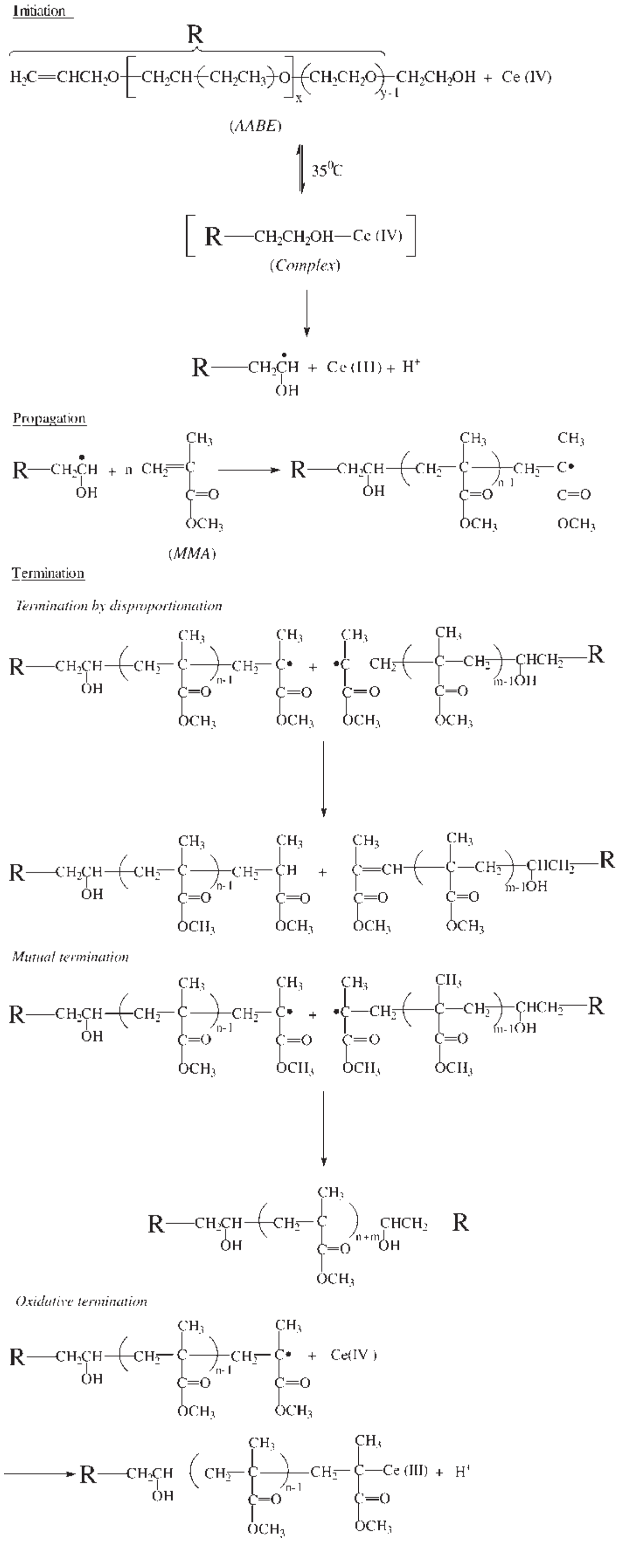
Methyl methacrylate (MMA) was supplied by Merck and purified by the usual methods. Allyl alcohol 1,2-butoxylate-*block*-etoxylate (AABE); Hydrophilic-Lipophilic Balance (HLB) = 6.9, melt point (m.p.) = 298 K, density (d) = 1.010 g/mL, refractive index (n_D) = 1.4610, tetrahydrofuran (THF) and nitric acid (HNO_3) were supplied by Aldrich and used as received. Methanol and toluene were supplied by Merck and used as received. Stock solutions of Ce(IV) were prepared from cerium(IV) ammonium nitrate (CAN) in aqueous nitric acid. CAN was supplied by Fluka and used as received. In all experiments, doubly distilled water was used as a continuous polymerization medium.

2.2 Polymerization Procedure

All the polymerization experiments were carried out in pyrex tubes. The reaction tubes were covered completely with thick foil, thus polymerizations were carried out in the absence of light. Polymerization was carried out as described in the earlier article (21).

From the relations between the experimental conditions, gel permeation chromatography (GPC) chromatograms, FTIR spectra and viscometry results of the samples, the following reaction scheme (Scheme 1) is suggested;

Firstly, Ce(IV)/AABE reaction occurs and free radicals are generated. These free radicals initiate the polymerization of MMA. Termination of growing chains by disproportionation, the combination themselves (mutual termination), Ce(IV) (oxidative termination), or by chain transfer is possible.



Sch. 1. The overall process for the polymerization of Allyl alcohol 1,2-butoxylate-*block*-etoxylate with methyl methacrylate.

The following Mark-Houwink parameters for PMMA (in toluene) were used in order to obtain the viscosity-average molecular weight; M_v; $K = 7.1 \times 10^3$ dL/g, $a = 0.73$ (K and a are constants, the values of which depend on the nature of the polymer and solvent, as well as on temperature).

The molecular weight, M_w, of AABE determined by GPC as 1970 g/mole ($M_n = 1690$ g/mole) and molecular weight (M_v) of the copolymers were determined by the viscometry method as; 0.21×10^4, 0.6×10^4, 2.1×10^4, 26.7×10^4, 18.7×10^4 and 11.4×10^4 g/mole at 298, 308, 313, 323, 333 and 343 K, respectively.

2.3 Dielectric Measurements of the Copolymer Samples

An LCR meter, HP 4284A model, was used to measure the dielectric properties of the copolymers. The copolymers were dissolved in THF and poured into Petri dishes and waited for evaporation of the solvent for 24 h. Then, each sample was put in an oven thermostated at 323 K for 24 h. Thereafter, films with the diameter of 6 mm were taken out from each AABE-*b*-PMMA copolymer film. The films were painted by silver paste, and electrodes were positioned on each surface. The dielectric constant values were recorded in the frequency range from 100 Hz to 1 MHz frequency and in the temperature range of 80–400 K. The medium temperature was controlled under vacuum (10^{-5} mbar) with an Oxford ITC 502 model temperature controller and liquid nitrogen cryostat.

3 Results and Discussion

AABE-*b*-PMMA copolymers were synthesized at different temperatures, over the 298–343 K range. Molecular weight (M_v) of the copolymers was determined by the viscometry method. The dielectric constant (ε') of AABE-*b*-PMMA copolymers and pure PMMA ($M_v = 2.25 \times 10^5$ g/mole) at 1 kHz are presented in Figure 1. The dielectric constants of all samples did not vary with the temperature between 80 and 250 K. The dielectric constant exhibits a much faster increment with further increasing temperature above 300 K. This is the typical behavior in the transition region for the polymers having dipolar structure. In the transition region, the variation rate of the dielectric constant values with the temperature was the highest in the case of the copolymers which were prepared at 308, 313, and 323 K. All samples showed a different rate of change in their dielectric constants with the temperature, in the transition region. It was observed that the dielectric constants show a very small change up to 250 K, whereas ε' values changed with the polymerization temperature. The effect of the polymerization temperature on the dielectric constant and its temperature dependency reveals that polymerization temperature changes the number of dipoles per unit volume. Above the glass transition temperature of PMMA, the variation rate of the dielectric constants of the copolymers which were prepared at 308, 313 and 323 K reveal a sudden increment with increasing the free volume due to the temperature. This behavior is due to (i) the easier orientation of the dipole groups and (ii) the increasing the number of the oriented dipole groups of the AABE and PMMA segments. Moreover, at low temperature, the primary contribution to the dielectric constants is due to the dipole groups of the AABE segments.

The presence of different dipole groups and the number of the different segment fractions in the polymers affect the dielectric constant. This effect can be seen clearly in Figure 1.

Figure 2 shows the dependence of the dielectric constant with the polymerization temperature at different ambient temperatures; 150, 250, 300 and 350 K. The dielectric constants show an increase up to 313 K, a decrease between 313 and 333 K, and then again an increase trend above 333 K for all studied polymerization temperatures. The observed changing dielectric constants depending on the polymerization temperature were attributed to the different dipole moment densities in the copolymers due to different segment composition. On the other hand, varying of the dielectric constant with medium temperature for a single polymer sample was attributed to the temperature dependence of the orientation activity of the dipole groups in the copolymers (Figure 1). The obtained very higher dielectric constants for the copolymers compared to those of pure PMMA were attributed to the higher quantity of AABE segments which have more dipolar structure than PMMA. The main effect to the dielectric constant arises from the AABE segment in the copolymer due to its C-O and OH dipoles. The highest

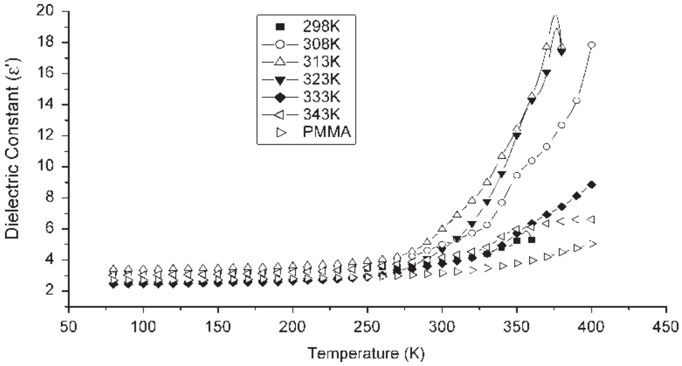


Fig. 1. Dielectric constant of the copolymers vs. medium temperature at 1 kHz.

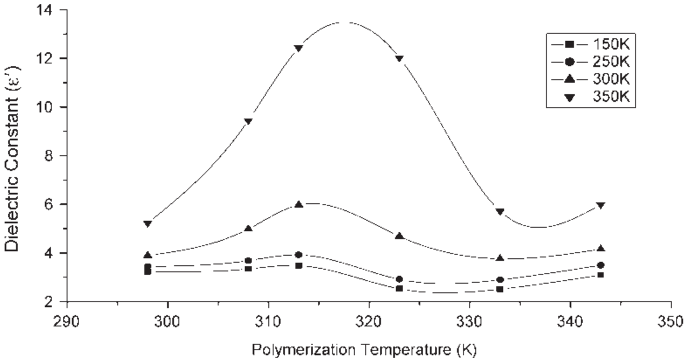


Fig. 2. Dielectric constant vs. polymerization temperature for different medium temperatures at 1 kHz.

dielectric constants in all studied temperatures for the copolymer prepared at 313 K and the decreases in the dielectric constants for the copolymers prepared above 313 K was attributed to the different dipole moment density in the copolymers due to the different AABE and PMMA segment fractions. The pronounced decreases in the dielectric constants for the copolymers, which were prepared at 323 and 333 K, were attributed to the increased segment quantity of PMMA, which has lower polar density than AABE. The higher PMMA segment quantity, which caused a lower dielectric constant at higher temperatures (323 and 333 K) was explained by two effects: (1) the increased viscosity of the polymerization system, which creates small MMA molecules more active than large AABE macromolecules for propagating active center and (2) degradative chain transfer, which is the characteristic of the allylic compounds and operative at higher temperatures. Allylic radicals are too stable to initiate polymerization and the propagating chain also terminates when transfer occurs, especially at higher temperatures. Thus, higher polymerization temperatures cause the higher PMMA segment quantity in the copolymer composition.

The frequency dependence of the dielectric constants for AABE-*b*-PMMA copolymers at 300 K is shown in Figure 3. The highest dielectric constant was observed in the case of the copolymer which was prepared at 313 K, in all frequencies. The lower dielectric constant for the copolymer which was prepared at 323 K, even with higher molecular weight, was attributed to the higher segment quantity of PMMA in the copolymer composition with lower dipolar groups. The decreasing of the dielectric constant with increasing frequency can be explained by frequency dependency of orienting dipoles. The orientation moment is fully established at low frequencies and therefore, dielectric constant reaches its maximum values. On the other hand, at higher frequencies, the dipoles will not have enough time to orientate and thus, the dielectric constant decreases. The dielectric constants again show an increase trend above 333 K. This behavior can be explained by the polymer chain length. The copolymers have shorter chains with a smaller PMMA segment fraction due to the earlier termination because of the increasing side reactions above 333 K.

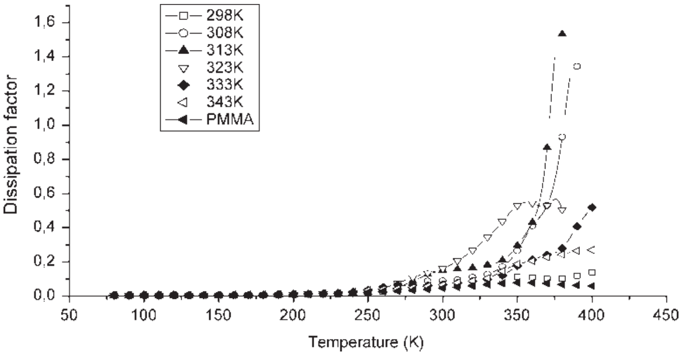


Fig. 4. Dissipation factor of the copolymers versus medium temperature at 1 kHz.

Figure 4 shows the temperature dependence of the dissipation factor at 1 kHz for all samples. A relaxation with the maximum dissipation factor was observed at 350 K for pure PMMA. Similarly, a maximum dissipation factor was observed at 360 K for the copolymer which was prepared at 323 K. However, attention should be paid to the intensity of the peak so that, it is 7 times higher than that of pure PMMA. Therefore, we can conclude that the copolymer sample includes not only a AABE segment, but also high PMMA segment quantity. The copolymers, which were prepared at 308 and 313 K showed a very high increment in dissipation factor in the PMMA relaxation region, but without any relaxation. This sudden increment was entirely attributed to the larger AABE segment and its activated dipole groups, whose tendency leans toward the orientation polarization. The absence of the relaxation peaks for the two copolymers could be attributed to the very low PMMA segment quantity in the copolymers.

Figure 5 shows the dependence of the dissipation factor to the polymerization temperature at three different temperatures as; 250, 300 and 350 K. As can be seen in Figure 5, all the copolymers have a nearly stable dissipation factor at 250 K and the dissipation factor is not affected by the polymerization temperature. The reason being, that the polar groups of the copolymers cannot orient and absorb energy in the applied electric field because of the frozen

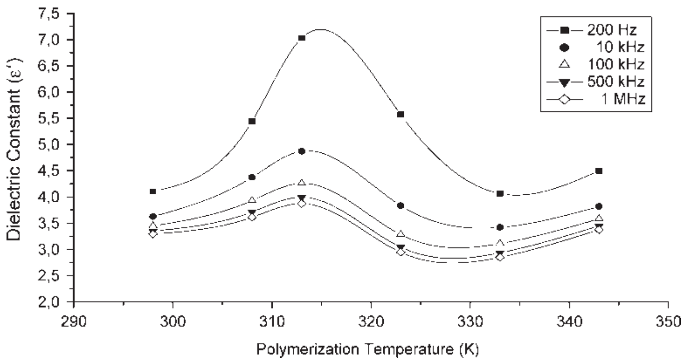


Fig. 3. Dielectric constant vs. polymerization temperature for 200 Hz, 10 kHz, 100 kHz, 500 kHz and 1 MHz at 300 K.

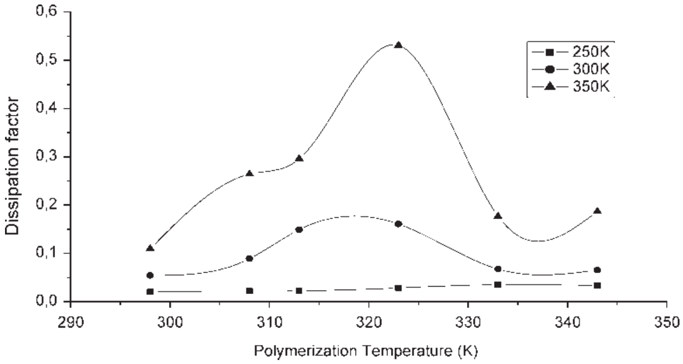


Fig. 5. Dissipation factor of the copolymers vs. polymerization temperature for different temperatures at 1 kHz.

molecular chain segments. But, as the temperature approaches, the glass transition temperature of PMMA, dipole groups of PMMA and AABE segments which were tightened with PMMA chain entanglements start to move by increasing the free volume. The dipoles can orient easily due to the freely chain movement and increase the number of dipoles per unit volume and thus dielectric constant (Figure 1). The highest dissipation factors were observed for the copolymer which was prepared at 323 K (Figure 5) because of the larger PMMA segment and thus, higher medium viscosity and higher hindrance to the orientation. The copolymer which was prepared at 323 K shows a lower dielectric constant close to the transition temperature of PMMA compared to the copolymer, which was prepared at 313 K (Figure 2). This is due to the higher PMMA content of the copolymer which was prepared at 323 K rather than 313 K. On the other hand, the observed lower dissipation factor even with the higher dipole moment for the copolymer, which was prepared at 313 K, was attributed to the lower PMMA content and thus, lower hindrance to the orientation.

The dependency of the molecular weight and the dissipation factor values (obtained at 350 K) of the copolymers on the polymerization temperature are presented in Figure 6. The dependence of the dissipation factor on the polymerization temperature is very similar to the dependence of the molecular weight on the polymerization temperature. The highest molecular weight gave the highest dissipation factor. The higher dissipation factors were attributed to the higher segment quantity of PMMA in the copolymers.

The quantitative copolymer composition was determined by IR spectroscopy, which is one of the possible procedures to compare the obtained qualitative compositions. The quantitative copolymer composition was investigated by comparison of the intensity of carbonyl group (C=O) of PMMA units to the end hydroxy group (-OH) of AABE units. The ratios of the absorption intensities of C=O groups of PMMA units ($\sim$1730 cm^{-1}) to -OH groups of AABE units ($\sim$3520 cm^{-1}) were calculated [polymerization temperature/log$_{10}$ I_{1730}/I_{3520}: 298/1.30, 308/3.29, 313/4.88, 323/7.50, 333/1.22, 343/1.03]. It was found that the PMMA content increases up to polymerization temperature of 323 K and then decreases.

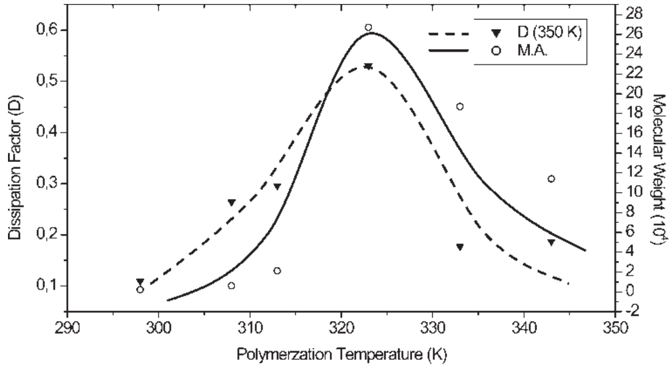


Fig. 6. Dissipation factor (at 350 K) and molecular weight of the copolymers vs. polymerization temperature at 1 kHz.

AABE-*b*-PMMA copolymers were prepared at 298, 308, 313, 323, 333 and 343 K, and the composition of the copolymers was qualitatively evaluated by the dielectric measurements and compared to those of the quantitave results, which were obtained by IR spectroscopy. The qualitative and quantitative results are in good agreement. It was clarified, that the copolymers contain more AABE segment than PMMA segment when prepared up to 313 K and the highest dielectric constant was obtained at 313 K. The PMMA segment quantity reached the maximum level for the copolymer which was prepared at 323 K and therefore, lower dielectric constant and higher dielectric loss were observed. The dipole groups of PMMA segments cannot rotate easily because of the higher medium viscosity. Above 323 K, the copolymers contain shorter chain length with a shorter PMMA segment due to the earlier termination because of the side reactions at higher temperatures. In that case, the dielectric constants trend to increase.

4 Conclusions

Redox initiated free-radical polymerization of methyl methacrylate (MMA) with allyl alcohol 1,2-butoxylate-*block*-etoxylate (AABE) was carried out to yield AABE-*b*-PMMA copolymers over the 298–343 K range. The composition of the copolymers, depending on the polymerization temperature, was qualitatively estimated by the dielectric measurements. The effect of the medium and polymerization temperature and the frequency on the dielectric constant and dissipation factor of the copolymers was discussed. It was found that the magnitude of the dielectric constant and its temperature dependency is directly affected by the polymerization temperature. There was almost no effect of the medium temperature on the dielectric constant of the copolymers below 250 K. but there were some changes in the dielectric constant values compared to those of pure PMMA. There was no any change in the dielectric constants with the temperature below the transition temperature of PMMA because of the frozen dipole groups.

The main effect to the dielectric constant at lower temperatures, when all segments are in glassy state, arises from the dipole groups, located parallel to the field. The observed different dielectric constant, even at lower temperatures for the copolymers, which were prepared at different polymerization temperatures, indicates the effect of the polymerization temperature. The highest variation rate of the dielectric constant with the temperature was found as 0.1126 K^{-1} for the copolymer which was prepared at 323 K. The fast increment for the copolymer which has the highest PMMA segment quantity was explained by the abrupt movement of the PMMA segment and the orientation ability of the dipole groups of the AABE and PMMA segments. The highest dielectric constant was obtained at 300 K medium temperature for the copolymer which was prepared at 313

K. The highest dissipation factor and relaxation was observed at 350 K and 1 kHz frequency for the copolymer which was prepared at 323 K. Copolymers which were prepared at 308 and 313 K, showed high dielectric loss without any relaxation transition. The dependency of the dielectric constant on the polymerization temperature was very similar to that of the dependence of the molecular weight on the polymerization temperature. The quantitative copolymer composition was determined by IR spectroscopy and the results were in good agreement with the qualitative results, which were obtained by the dielectric measurements. Finally, we can conclude that the qualitative composition of the copolymers can be evaluated by the dielectric measurements.

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