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DIELECTRIC PROPERTIES OF BLOCK COPOLYMERS OF ETHYL METHACRYLATE WITH STYRENE

ABSTRACT

The dielectric properties of all polymers were calculated over the frequency range 1 kHz−2 MHz at room temperature and submitted as in compared with each other. The dielectric constant of homo, diblock and triblock copolymers, [poly(EMA), poly(EMA-b-St), poly(EMA-b-St-b-EMA), respectively], were determined as 4.58; 4.07; 3.68 at 1 kHz and as 4.25; 3.89; 3.44 at 2 MHz, and the decrease ratio in dielectric constants were found as 7.02%, 6.5%, 4.4%, respectively. The magnitude of resistance decreased with increasing frequency while the magnitude of reactance increased. After a certain frequency (about 400 kHz), both of these parameters tended to a constant trend. Especially, at low frequencies (1-50 kHz) the AC conductivity rapidly increased. The increasing tendency of AC conductivity for all polymers was determined as similar to each other.

Keywords: Dielectric Constant, Capacitance, Resistance,
AC Conductivity, Polymers

ETİL METAKRİLAT’IN STİREN İLE BLOK KOPOLİMERLERİNİN DİELEKTRİK ÖZELLİKLERİ

ÖZET

Bütün polimerlerin dielektrik özellikleri oda sıcaklığında 1kHz−2MHz frekans aralığında ölçüldü ve birbirleri ile karşılaştırılmalı olarak verildi. Poly(EMA) homopolimerinin, poly(EMA-b-St) ve poly(EMA-b-St-b-EMA) blok kopolimerlerinin dielektrik sabit değerleri 1 kHz’de 4.58, 4.07, 3.68; 2 MHz’de 4.25, 3.89 ve 3.44 olarak belirlendi. Dielektrik sabitlerindeki düşme oranı ise sırasıyla %7.02, %6.5, %4.4 olarak hesaplandı. Reaktansın büyüklüğü artan frekans ile azalırken rezistansın büyüklüğü ise artan frekansla artmaktadır. Belirli bir frekans değerinden sonra (yaklaşık 400 kHz), bu iki değerin herikisi de sabit bir değere ulaşmaktadır. Özellikle, düşük frekans değerlerinde (1-50 kHz) AC iletkenlik türünün artma eğiliminin bütün polimerler için benzer bir yaklaşım sergilediği belirlendi.

Anahtar Kelimeler: Dielektrik Sabiti, Kapasitans, Rezistans,
AC İletkenlik, Polimerler

1. INTRODUCTION (GİRİŞ)

In the recent years, the electrical conductivity, optical and dielectrical properties of polymers have been extensively investigated The dielectric characteristics of a material are the most important properties when considering the use of a particular material in capacitor applications or in actuator or transducer applications. Polymer dielectrics are that they tend to be lightweight, flexible, and easily processed. Thus, these polymers, used in the construction of capacitors and actuators, seem to be a class of materials that can potentially show the best overall performance in a variety of categories, including electrical energy density, maximum strain capability, elastic energy density, and efficiency.

Dielectric properties in polymers are due to electronic, ionic, molecular and interfacial polarization. These properties are associated with the physical and chemical structure of the polymers. Polymer materials can be characterized by their electrical parameters such as dielectric constant, conductance and admittance, etc. using various experimental methods such as dielectric spectroscopy and direct current (DC)-alternating current (AC) conductivity techniques [1-4]. These parameters change with frequency. In the dielectric experiments, when an AC is applied to a solid, it produces an alternating electric polarization. So, it is well-known that the complex field and displacement are given by

$$E^* = E_o \exp(i\omega t) \tag{1}$$

$$D^* = D_o \exp(i\omega t - \delta) \tag{2}$$

Furthermore,

$$D^* = \varepsilon^* E^* = (\varepsilon' + i\varepsilon'')E^* \tag{3}$$

where ε' and ε'' are the real and imaginary parts of the complex dielectric constant The real part of the dielectric constant, most often referred to with the word "real" omitted, is the quantity that describes electrical energy converted into stored potential energy, generating a polarization of the dielectric material. This energy storage process is always accompanied by a loss current. This represents energy that is not stored, but is dissipated within the material in the form of heat.

2. RESEARCH SIGNIFICANCE (ÇALIŞMANIN ÖNEMİ)

In this article, the dielectric properties of poly (EMA), poly(EMA-b-St) diblock and poly(EMA-b-St-b-EMA) triblock copolymer were reported. For this purpose, dielectric measurements were carried out using pellets with thickness ranging from 1 mm to 1.5 mm and a diameter 6 mm in pressed under 5 ton/cm^2. Two probes of copper wire were used. The dielectric parameters of polymers were performed by means of a Quadtech 7600 LCR meter over the frequency range 1 kHz–2 MHz. All measurements have been performed at room temperature, with high accuracy (1% typ.)

3. EXPERIMENTAL METHOD (DENEYSEL YÖNTEM)

3.1. Materials (Malzemeler)

Ethylmethacrylate (EMA) (Aldrich) and Styrene(Aldrich) were distilled under vacuum after washing with 5% NaOH aqueous solution just before homo and copolymerization. Cuprous bromide (CuBr), 2,2$'$-bipyridyne and ethyl 2-bromo acetate (2-EBA) (analytical reagent) were used as received.

3.2. Instrumental Techniques (Enstrümental Teknikler)

Infrared spectra were obtained on a Mattson 1000 FTIR spectrometer and obtained by polymeric film or liquid film on a salt plate. NMR spectra were recorded on a Jeol FX 90Q NMR spectrometer at room temperature using $CDCI_3$ as a solvent and TMS as an internal standard. Dielectric measurements were carried out using pellets with thickness ranging from 1 mm to 1.5 mm and a diameter 6 mm in pressed under 5 ton/cm^2. Two probes of copper wire were used. The dielectric parameters of polymers were performed by means of a Quadtech 7600 LCR meter over the frequency range 1 kHz–2 MHz. All measurements have been performed at room temperature, with high accuracy (1% typ.).

3.3. Atom Transfer Radical Polymerization (Atom Transfer Radikal Polimerizasyonu)

For homo polymerization of EMA the catalyst, copper(I) bromide and ligand 2,2$'$-bipyridyne were first placed in a round bottom flask and three cycles of nitrogen pressurization followed by vacuum were applied to remove air and moisture from the flask. The deoxygenated monomer and initiator, ethyl methacrylate and ethyl 2-bromo acetate (2-EBA), was added into flask, respectively. The mixture was stirred at room temperature until it becomes homogeneous. The flask was placed in an oil bath at 110°C. After the polymerization had carried out, the flask was removed from oil bath and the reaction mixture was dissolved in chloroform, filtered, and the polymer was precipitated in methyl alcohol with 1% aqueous hydrochloric acid, and dried at 45°C. The same procedure and amount of chemicals for synthesizes of poly(EMA-b-St) diblock and poly(EMA-b-St-b-EMA) triblock copolymer were applied except of macro initiators and polymerization temperatures. While the diblock copolymer of poly(EMA) with St was synthesized at 130°C using poly(EMA) as macroinitiator, the triblock copolymer of poly(EMA-b-St) with EMA was synthesized at 110°C using poly(EMA-b-St) as macroinitiator. The molar ratio of compounds in this polymerization system were applied as 1:1:2:100 for initiator(or macroinitiators):Cu(I)Br:bpy: monomers, respectively.

4. RESULTS AND DISCUSSION (BULGULAR VE TARTIŞMA)

The characterization was confirmed by FT-IR and ^{1}H-NMR techniques. The most characteristic FT-IR absorption bands for poly(EMA) were attributed to the band at 1727 cm^{-1} for C=O ester group stretching, at 1455-1413 cm^{-1} for aliphatic C-H bending, at 1150 and 1030 cm^{-1} for asymmetric and symmetric C-O stretching, respectively. These bands were also observed for diblock and triblock copolymer except that the band at 1605 cm^{-1} for C=C stretching on aromatic ring in St units, which was appeared in diblock and triblock copolymer but wasn't seemed in homopolymer. ^{1}H-NMR spectra (Figure 1) for diblock and triblock copolymers show signals at 7.06-6.36 ppm (aromatic ring protons in St units), 4.12 ppm ($-COOCH_2$ protons in EMA units), 1.87-1.25 ppm (CH_3 , CH_2 and CH protons in main chain), 0.92 ppm (CH_3 protons in EMA units). Especially, the signal at 4.12 ppm attributed to $-COOCH_2$ protons in EMA units was observed as a weak intensity in poly(EMA-b-St) while it was middle in poly(EMA-b-St-b-EMA). Similar to this approach the signals at 7.06-6.36 ppm were observed as a strong intensity in diblock copolymer.

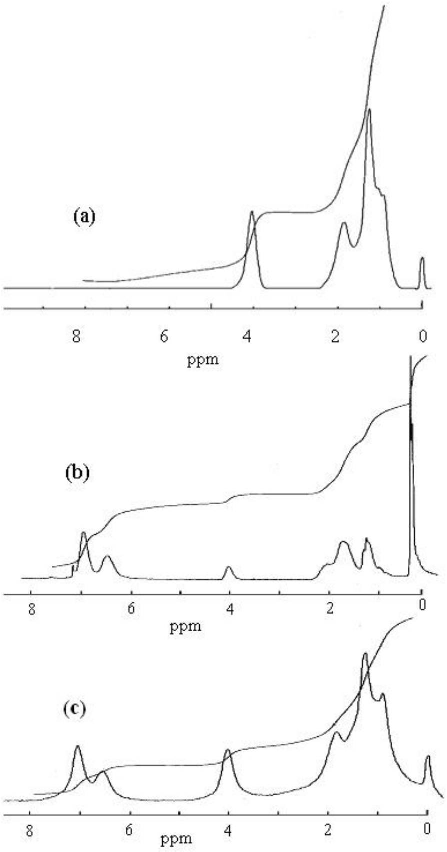

Figure 1. ^{1}H-NMR spectra of a) homopolymer b) diblock and c) triblock copolymers
(Şekil 1. a) homopolimer b) diblok ve c) triblok kopolimerlerin ^{1}H-NMR spektrumları)

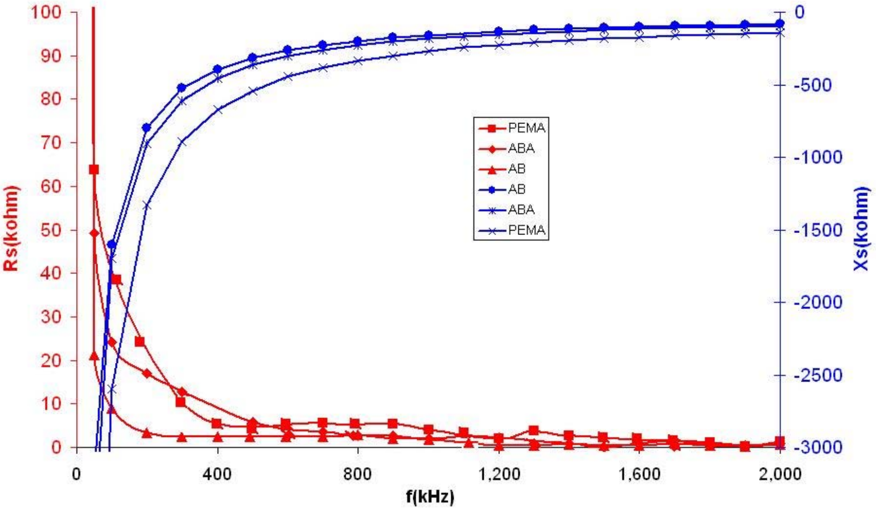

Figure 2. The real and imaginary parts of the impedance as a function of frequency
(Şekil 2. İmpedansın reel ve sanal kısımlarının frekansın bir fonksiyonu olarak değişimi)

4.1. The Frequency Dependence on Impedance (İmpedans Üzerine Frekansın Etkisi)

The real and imaginary parts of the impedance as a function of frequency for homo and block copolymers were illustrated in Figure 2. The complex impedance for a polymer is described as:

$$Z = R + iX \qquad (4)$$

where R is the real part, i.e, resistance and X is the imaginary part, i.e, reactance. It is seen that the resistance decreases while reactance increases with frequency. After a certain frequency (about 400 kHz), both parameters tend to a constant trend. Also, it is seen that the resistance values at low frequencies decreases from poly(EMA) homopolymer to poly(EMA-b-St) diblock copolymer. On the contrary, the magnitude of reactance values shifts from diblock copolymer towards homopolymer. Both parameters for poly(EMA-b-St-b-EMA) triblock copolymer are between homo and diblock copolymer.

4.2. The Frequency Dependence on Capacitance and Dielectric Constant (Kapasitans ve Dielektrik Sabiti Üzerine Frekansın Etkisi)

Figure 3 shows the frequency dependence of the capacitance and the dielectric constant for polymers. It is well-known that the dielectric constant is expressed as $\varepsilon = Cd/\varepsilon_0 A$ [5]. Where ε is the dielectric constant, C is capacitance, d is the thickness, A is the effective area, ε_0 is the permittivity of free space ($\varepsilon_0 = 8,854.10^{-12}$ $C^2 j^{-1} m^{-1}$).

From this figure, it is clear that ε decreases with increasing applied frequency. The dielectric constant at 1kHz and room temperature for poly(EMA), poly(EMA-b-St-b-EMA) and poly(EMA-b-St) were found as 4.58; 4.07; 3.68 and at 2 MHz as 4.25; 3.89; 3.44, respectively. Among these polymers, poly(EMA) has the highest dielectric constant value (ε =4,58). The reason of this result probably may be owing to effect of carbonyl group in the EMA units to molecular polarity. Also, the decrease ratio in dielectric constants at applied frequencies between 1 kHz and 2 MHz for homo, diblock and triblock copolymer are 7.02%, 6.5%, 4.4%, respectively. In general, this tendency in ε is reported by some workers for low frequencies [6 and 7]. Some more rapid decrease in ε values may be seen over the low frequency range 1-250 kHz. This may be due to the tendency of induced dipoles in the macromolecules to orient themselves in the direction of the applied field in this frequency range.

Towards higher frequency range the decreases in ε is slower and but steady, and this means that the dipoles will hardly be able to orient themselves in the direction of field. In conclusion, the high dielectric constant values at low frequencies can not be attributed to a single factor. Both electrode and interfacial polarizations may be presented. Contrarily, towards the higher frequency values this tendency shifts to increase of dielectric constant due to the fact that the polarization is caused by the alternating accumulation of charges at interfaces between different phases of the polymers. The electrical relaxation in the dielectric spectra doesn't observe due to orientation polarization of dipoles. At high frequencies, the periodic reversal of the dielectric field occurs so lower that there is excess charge diffusion in the direction of the field. That is why an increase in the permittivity or dielectric constant occurs due to charge accumulation [8].

4.3. The Frequency Dependence on Susceptance and AC Conductivity (Susseptans ve AC İletkenlik Üzerine Frekansın Etkisi)

The plots of the susceptance, Bp, and the AC conductivity, logσ (S/cm), plotted versus frequency were illustrated in Figure 4. If all polymers are compared with, it can be seen that the tendency increasing of AC conductivity for all polymers is similar to each other. At low frequencies (1-50 kHz) the conductivity rapidly increases, whereas it remains fixed towards the high frequencies. The AC conductivity at 1 kHz for poly(EMA), poly(EMA-b-St-b-EMA) and poly(EMA-b-St) are $6,07.10^{-8}$(S/cm); $1,04.10^{-7}$(S/cm); $1,21.10^{-7}$(S/cm) and at 2 MHz as $3,66.10^{-4}$(S/cm); $4,62.10^{-4}$ (S/cm); $5,99.10^{-4}$ (S/cm), respectively. The increase ratio in conductivity at applied frequencies between 1 kHz and 2 MHz for homo, diblock and triblock copolymer are about 6.10^{4}%; 5.10^{4}%; 4.10^{4}%, respectively. At low frequencies, the conductivity values of polymers are of the order of μS but at the high frequencies these values are mS. From these results, it can be said that these polymers are effected from applied field. The electrical charge centers move and electrical polarization occurs due to the fact that electrons and atoms orient in the effect of electrical field in the frequency range. Thus, formed electrical dipoles provide an electrical load accumulation on the polymer surface [9 and 10].

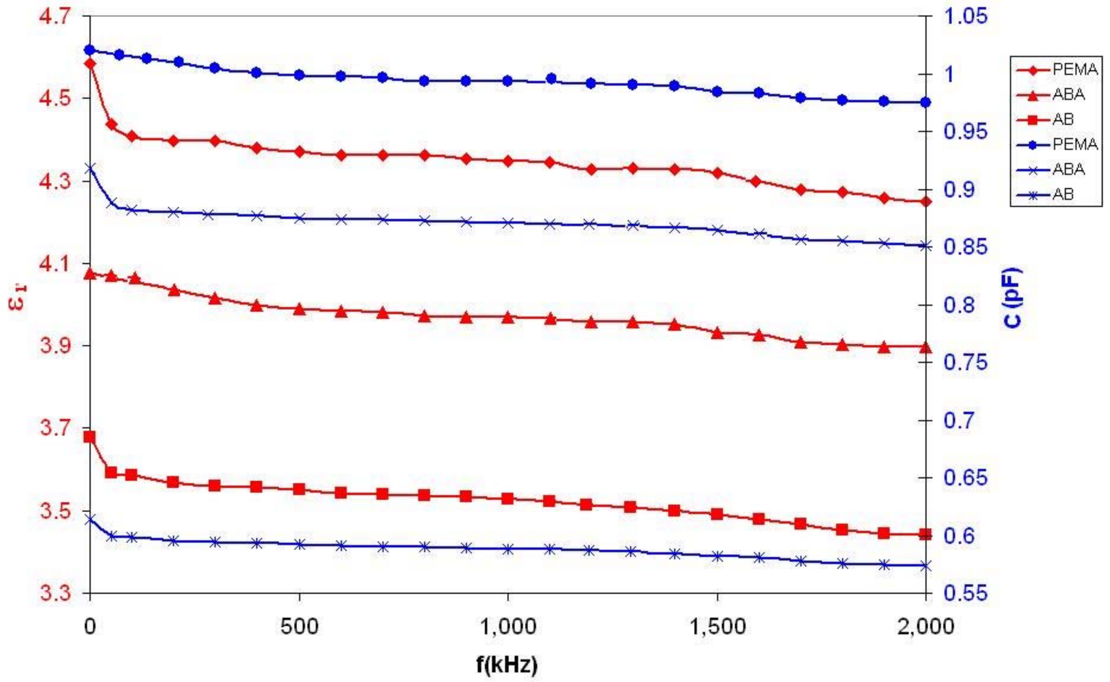

Figure 3. The capacitance and the dielectric constant as a function of frequency
(Şekil 3. Frekansın bir fonksiyonu olarak kapasitans ve dielektrik sabitinin Değişimi)

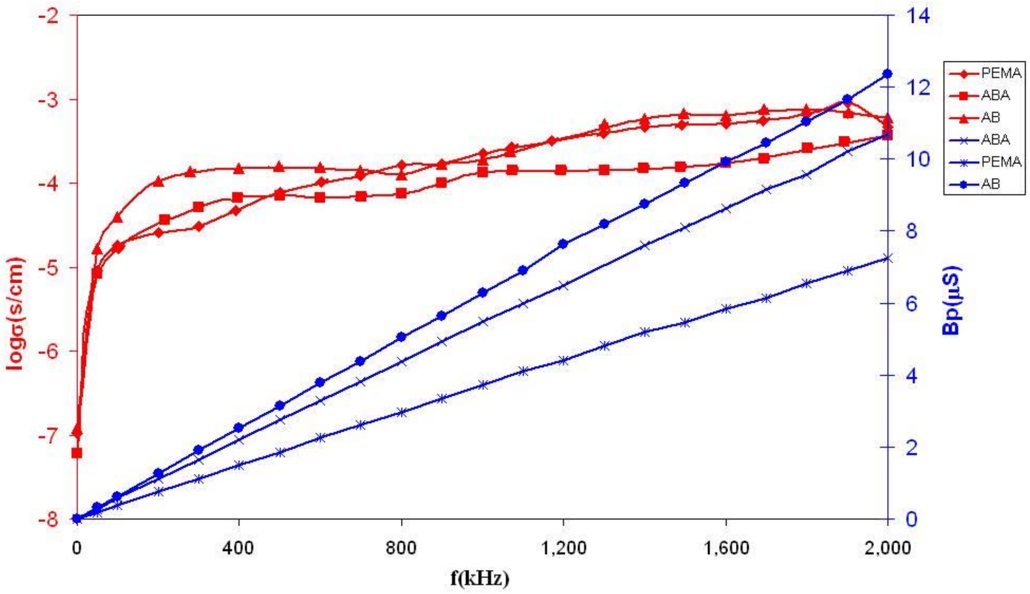

Figure 4. The susceptance and AC conductivity as a function of frequency
(Şekil 4. Frekansın bir fonksiyonu olarak susseptans ve AC iletkenliğinin Değişimi)

5. CONCLUSIONS (SONUÇLAR)

The dielectric parameters of poly(EMA), poly(EMA-b-St-b-EMA) measured over the frequency range 1 kHz – 2 MHz at room temperature were determined and submitted as in compared with each other. The dielectric constant of homo, diblock and triblock copolymers were determined as 4.58; 4.07; 3.68 at 1 kHz and as 4.25; 3.89; 3.44 at 2 MHz, and the decrease ratio in dielectric constants were found as 7.02%, 6.5%, 4.4%, respectively. At low frequency range, it was said that a more rapid decrease in ε values may be due to the tendency of induced dipoles in the macromolecules to orient themselves in the direction of the applied field. The magnitude of resistance decreased with increasing frequency while the magnitude of reactance increased. The AC conductivity rapidly increased especially at low frequencies (1-50 kHz). The increasing tendency of AC conductivity for all polymers was determined as similar to each other.

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