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Synthesis and Dielectric-Antimicrobial Properties of Poly(n-Butyl Methacrylate) with Chalcone Initiator

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Abstract

In this study, in the first stage, the chalcone compound was synthesized in accordance with the literature. Then, the synthesized chalcone compound was reacted with bromine acetylbromide and the initiator used in the ATRP method was synthesized. The characterization of the synthesized compound was carried out by FT-IR and NMR spectrometers. The number average molecular weight (Mn) of the polymer was measured as 11780 and the heterogeneity index (HI) was measured as 1.32 by Gel Permeation Chromatography (GPC). In the second stage, the synthesized chalcone compound was used as an initiator and the polymerization of n-butyl methacrylate monomer was provided by the ATRP method. In the last stage, the dielectric and antimicrobial properties of the polymer were investigated. The Agar well method was used in the antimicrobial study. Dielectric properties were investigated as a function of frequency between 100 Hz and 5000 Hz at room temperature.

Keywords: Chalcone; ATRP; Antimicrobial properties; Dielectric properties.

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Poli(n-Bütil Metakrilat)'ın Kalkon Başlatıcısı ile Sentezi ve Dielektrik-Antimikrobiyal Özellikleri

Öz

Bu çalışmada, ilk aşamada, literatüre uygun şekilde kalkon bileşiği sentezlenmiştir. Daha sonra sentezlenen kalkon bileşiği ile brom asetilbromür ile tepkimeye sokularak ATRP metodunda kullanılan başlatıcı sentezi gerçekleştirilmiştir. Sentezlenen bileşiğin karakterizasyonu, FT-IR ve NMR spektrometreleri ile yapılmıştır. Jel Geçirgenlik Kromatografisi (GPC) ile polimerin sayıca ortalama molekül ağırlığı (Mn) 11780 ve heterojenlik indisi (HI) ise 1.32 ölçülmüştür. İkinci aşamada, sentezlenen kalkon bileşiği başlatıcı olarak kullanılarak ATRP metodu ile n-bütil metakrilat monomerinin polimerleşmesi sağlanmıştır. Son aşamada ise polimerin dielektrik ve antimikrobiyal özelliği incelenmiştir. Antimikrobiyal çalışmada Agar kuyu yöntemi kullanılmıştır. Dielektrik özellikleri, oda sıcaklığında 100 Hz ile 5000 Hz aralığında frekansın bir fonksiyonu olarak incelenmiştir.

Anahtar Kelimeler: Kalkon; ATRP; Antimikrobiyal özellik; Dielektrik özellik.

1. Introduction

Polymers are high molecular weight compounds formed by the regular bonding of many molecules with chemical bonds [1]. Polymers are used as basic materials in many areas such as toy materials, textile materials, insulation materials, space vehicles, automobile parts, waste and clean water pipes, door and window materials, elastomers, foams, adhesives and many packaging materials. Many of the materials containing polymers have been the subject of research in many areas because they are cheap, lightweight, non-corrosive and durable materials [2]. Synthesis of functional polymers is very important in terms of technological developments. Synthesis of functional polymers is possible by polymerization of monomers with functional groups or by chemical modifications.

Chalcone compounds are one of the members of the flavonoid family that do not have a heterocyclic C ring. The presence of an α,β-unsaturated carbonyl group on the propane chain in the main structure of flavonoids, or in other words, the presence of a double bond and a ketone group, forms chalcones. Chalcone is used for all compounds with the structure of 1,3-diaryl-2-propen-1-one [3]. It is known that chalcones are found in edible plants and fruits in nature and are very beneficial compounds for health. They can be obtained from plants and fruits by methods such as extraction and can also be synthesized chemically. Cyclic compounds and their derivatives containing heteroatoms are used in many areas such as agriculture and medicine.

Polymers containing chalcone as a functional group have good thermal stability, solubility, photosensitivity and film formation capacity [4-6]. Polymers containing reactive functional groups are of great industrial and academic importance. The reason is that their synthesis is basically compatible with modification of the polymer structure to have the desired macromolecules in specific applications. Photopolymers are used to consider the properties of photosensitizers and macromolecular groups. Polymers with photocrosslinkable functional groups such as chalcones, thymine, and coumarin have become an active research area in the polymer world due to their technological importance in the fields of photolithography, non-linear optical materials, microelectronics, liquid crystal materials, and electrophotographic coating [7,8]. Chalcones and their derivatives possess various potent biological activities, such as antimicrobial [9,10], antihypertensive [11], anticancer [12], antioxidant [13], antidiabetic [14], anti-inflammatory [15], antiulcer [16], antimalarial [17], antiviral [18] and anti-gout [19].

AC conductivity measurements of materials are very important. When a dielectric material is placed between opposite poles, it reduces the force acting between the electric charges as if they were separated. Therefore, the dispersion and dielectric constant factor help us to obtain more information about the properties of the polymer. There are many studies on the electrical behavior of methacrylate and styrene derivatives [20-22]. In our study, the polymer containing the chalcone group in the end group was synthesized, and its dielectric properties were investigated.

In this study, it has been proven to be used in the polymerization reaction by synthesizing the previously synthesized but not used in the ATRP method, according to the literature. Thus, it has been determined that it could lead to new studies. investigating how the departure groups at the ends of the polymer chain will affect the polymers has a very high potential to lead new studies

2. Materials and Methods

2.1. Synthesis of 4-[3-(1-benzofuran-2-yl)-3-oxoprop-1-en-1-yl]phenyl bromoacetate

It was synthesized in accordance with the literature [23]. The synthesis reaction is shown in Fig. 1.

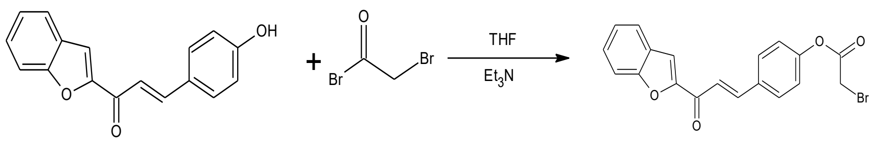


Figure 1: Initiator synthesis.

2.2. Polymer synthesis by ATRP method

0.07 mmol CuBr, 0.14 mmol Bpy and 0.07 mmol synthesized initiator were added to a rubber capped polymerization tube. Then, 1 drop of 1,4-dioxane solvent was dropped into this mixture. After the complex formation, 7 mmol of n-butylmethacrylate monomer was added to the polymerization tube and 0.5 ml of 1,4-dioxane solvent was added. The prepared polymer tube was passed through argon gas for ten minutes and then placed in an oil bath set at 110 ºC and kept for 24 hours. The polymerization was terminated after the polymer solution thickened. Then, the thickened polymer solution was dissolved in dichloromethane and precipitated in methyl alcohol. The precipitation process was repeated three times. The precipitated polymer was dried first at room temperature and then under vacuum at 40 ºC for 24 hours. The polymer reaction is shown in Fig. 2.

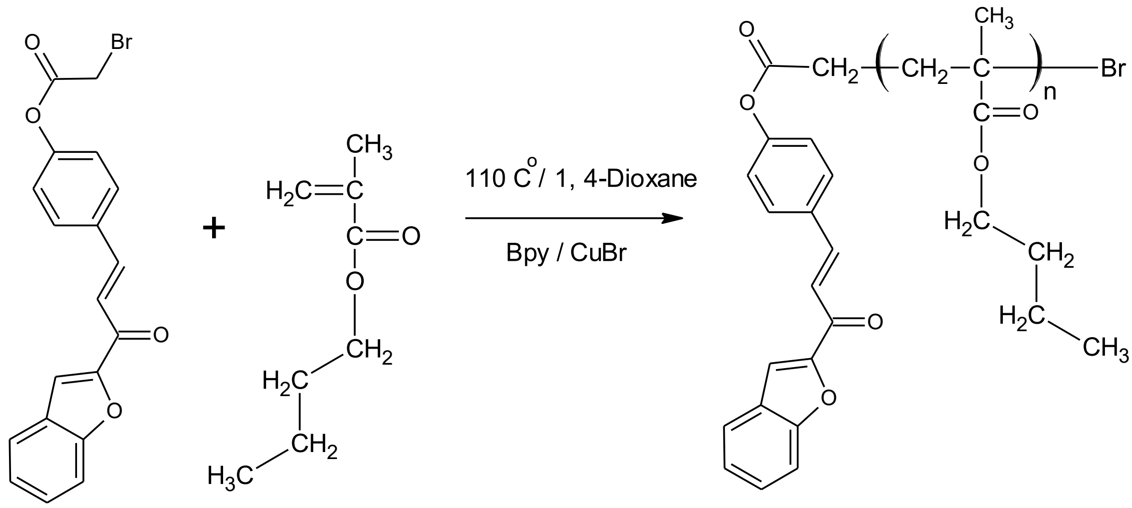


Figure 2: Polymer synthesis.

2.3. Dielectric measurements of polymer

The dielectric properties of the synthesized polymer were investigated. The polymer was converted into pellets by applying approximately 4 tons of pressure and the pellet thickness was measured. The pellet surfaces were painted with silver paint. The dielectric properties of the polymer were investigated as a function of frequency between 100 Hz and 5000 Hz at room temperature with the impedance analyzer.

2.4. Biological studies

In this study, the gram-negative bacteria Escherichia coli ATCC 25322 and Klebsiella pneumaniae ATCC 700603, Gram-positive bacteria Bacillus megaterium DSM32 and

Staphylococcus aureus ATCC 25923 and a fungus Candida albicans FMC17 were used. These microorganisms were obtained from Elazığ Fethi Sekin City Hospital Central Laboratory.

2.4.1. Antimicrobial Studies

An Agar well diffusion method was used to test the antimicrobial effects of the polymer on bacterial strains. Each bacterium was inoculated onto Sabouraud dextrose agar (SDA) and Nutrient Broth (Biolife Lot: HE2602) using a loop and adjusted to the McFarland turbidity standard of 0.5 to obtain a bacterial density of approximately 1-2 x 108 CFU/ml. The fungal strain was inoculated onto petri dishes containing SDA and incubated for 48 hours (31°C). Yeast colonies were suspended in 0.9% sodium chloride (saline) solution and incubated at 45°C to reach a concentration of 2x107 cells/ml. Diluted and sterilized in autoclave (121°C for 15 min) MHA was distributed in an 15-20 ml amounts into petri dishes and allowed to cool. 100 µl of microorganism suspension was added to the solidified MHA and spread evenly on the agar using a drigalski spatula. Wells of the desired diameter were opened with an agar piercer (corkborer). Samples were prepared at four concentrations (125, 250, 500 and 1000 mg/ml) and mixed under aseptic conditions at 100 µl per well. Incubation for bacteria and fungi inoculated plates was 24 h (37±0.1ºC) and 48 h (25±0.1ºC), respectively. 100% DMSO (Merc-Lot K51154243 948) was used as a negative control and a standard disk containing 2 mcg clindamycin (Lot 171127A) was used as a positive control. At the end of incubation, inhibition diameters were measured [24,25].

2.4.2. Determination of antioxidant activity

2,2-Diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity method was used to evaluate the antioxidant activity of the synthesized polymer. The stock solution of the polymer was prepared and then serially diluted with 0.005% methanolic DPPH solution at concentrations of 125, 250, 500, 1000 µM. 100% ascorbic acid was used as positive control, and 100% methanol was used as negative control. After the mixtures were incubated at 37±0.1°C for 30 min, their absorbances were measured by spectrophotometer at 517 nm wavelength. The following formula was used to determine the scavenging rate of DPPH radicals for each mixture [26]:

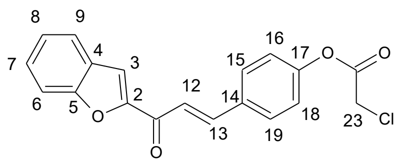
$$\text{Antioxidant activity (\%)} = [(\text{Ac} - \text{As}) \div \text{Ac}] \times 100 \quad (1)$$

Ac: Control absorbance; As: Sample absorbance.

3. Results and Discussion

3.1. Characterization of 4-[3-(1-benzofuran-2-yl)-3-oxoprop-1-en-1-yl]phenyl bromoacetate

The IR spectrum of the synthesized initiator is given in Fig. 3, the ^{1}H-NMR spectrum in Fig. 4 and its evaluation in Table 1.



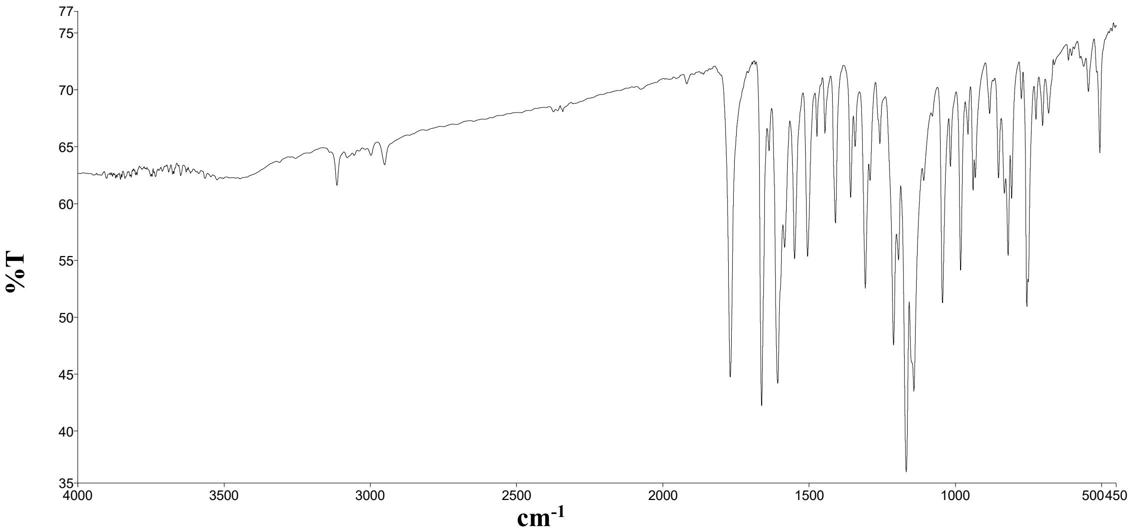


Figure 3: IR spectrum of the initiator.

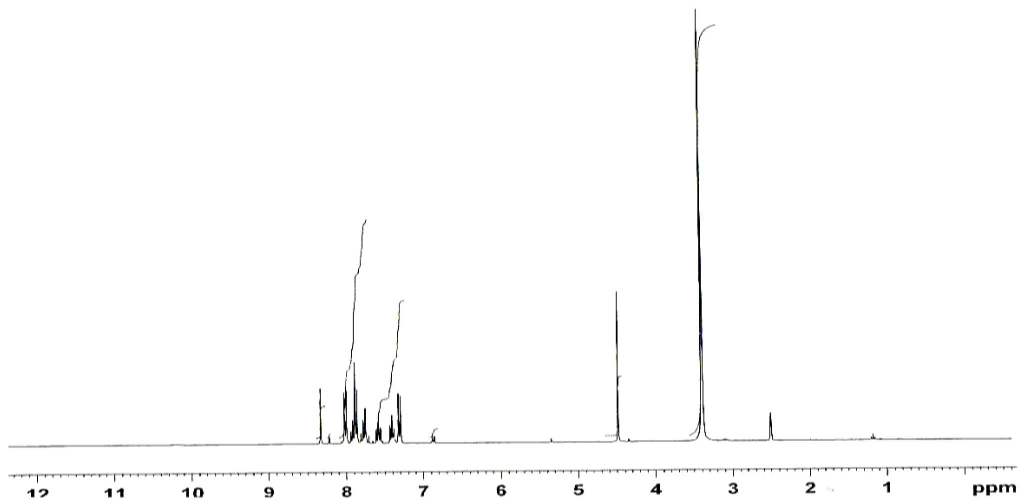


Figure 4: ^{1}H-NMR spectrum of the initiator.

Table 1: Spectrum evaluation of the initiator.

FT-IR (cm^{-1})			
3114-3000	Aro. C-H	1609	Aro. C=C
1761	C=O	1165	C-O-C asym.
1660	C=O (C=C-C=O)	1133	C-O-C sym.

^{1}H-NMR (ppm) DMSO-d_6									
H_3	**H_{19}**	**H_{13}**	**H_9**	**H_{12}**	**H_6**	**H_7**	**H_8**	**H_{18}**	**H_{23}**
8,31	8,02	7,92	7,89	7,83	7,75	7,55	7,41	7,31	4,49

3.2. Characterization of Polymer

The IR spectrum of the synthesized polymer is given in Fig. 5, the ^{1}H-NMR spectrum in Fig. 6, the GPC spectrum in Fig. 7 and its evaluation in Table 2.

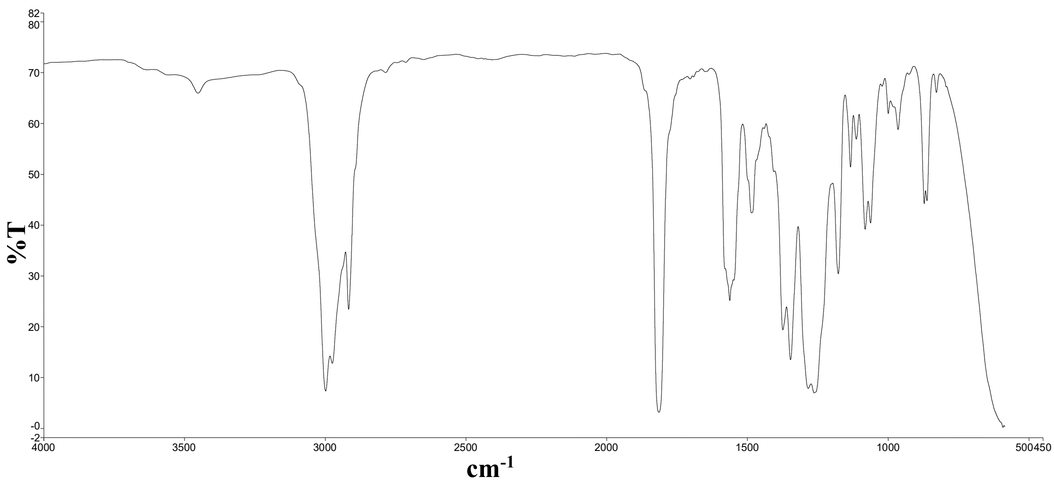


Figure 5: IR spectrum of the polymer.

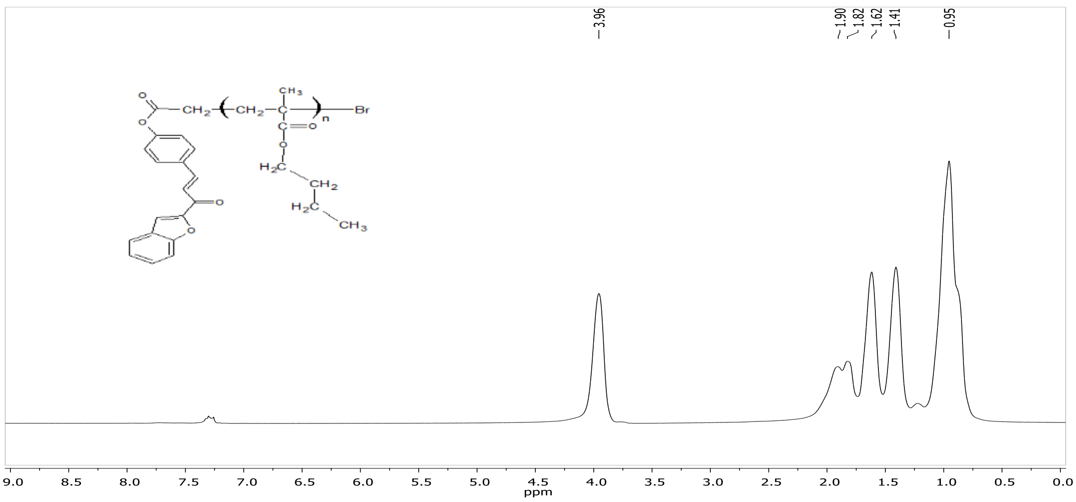


Figure 6: ^{1}H-NMR spectrum of the polymer.

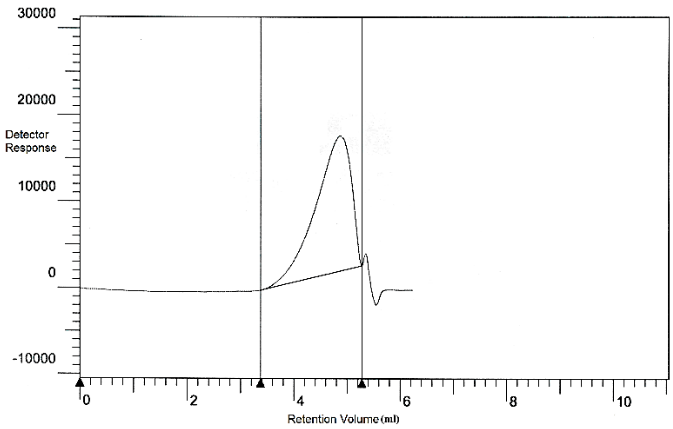


Figure 7: GPC spectrum of the polymer.

In the IR spectrum of the polymer synthesized by the ATRP method; aliphatic C-H stretching at 2945-2845 cm-1, ester C=O stretching at 1736 cm-1, C-H stretching at 1371-1393 cm-1 and C-O-C symmetric stretching in the range of 1148-1050 cm-1 and C-Br stretching at 670-500 cm-1 are the characteristic bands. In the ^{1}H-NMR spectrum; signals at 7.51-7.10 ppm characterize aromatic ring protons and solvent signals, signals at 3.96 ppm characterize O-CH_2 protons, signals at 1.90 ppm characterize CH_2 protons in the main chain and signals at 1.82-0.95 ppm characterize CH_2-CH_3 protons. Since aromatic protons are only at the ends of the chain, the signals are weak.

Table 2: Spectrum evaluation of the polymer.

FT-IR (cm^{-1})			
2945-2845	Ali. C-H	1148-1050	-C-O-C
1736	C=O	670-500	C-Br gerilmesi
1371-1393	C-H		
^{1}H-NMR (ppm) $CDCl_3$			
H Aromatic	**H** OCH_2	**H** CH_2 (Main chain)	**H** CH_3
7,51-7,10	3.96	1.90	1.82-0.95

3.3. Dielectric Results

The dielectric properties of the synthesized polymer were investigated. The polymer was converted into pellets by applying 4 tons of pressure and the pellet thickness was measured. The pellet surfaces were painted with silver paint. Measurements were taken at different frequencies with the impedance analyzer. Dielectric measurements of the polymer against frequency are shown in Fig. 8, Fig. 9 and Fig. 10. The dielectric values of the polymer at 1 kHz and room temperature are given in Table 3.

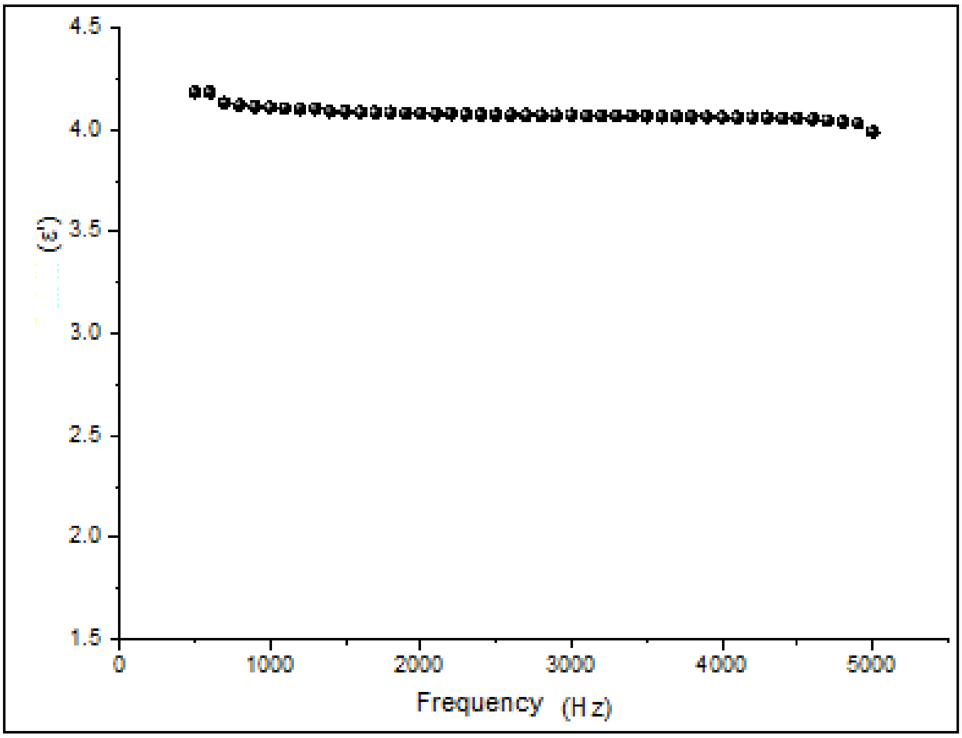


Figure 8: Variation of dielectric constant versus frequency.

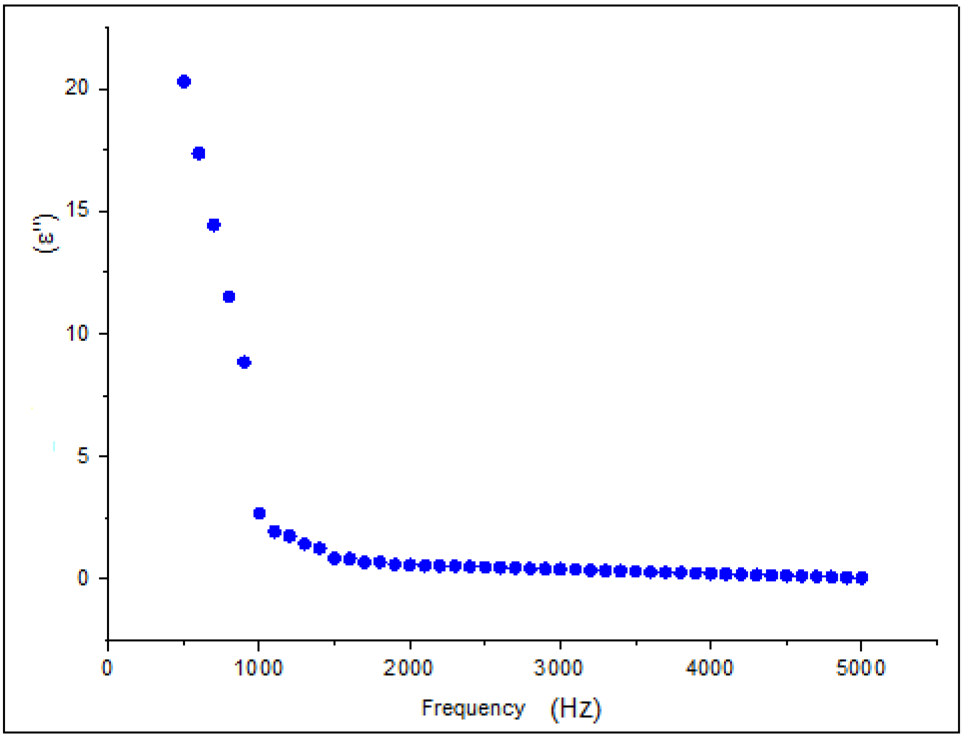


Figure 9: Variation of dielectric loss factor versus frequency.

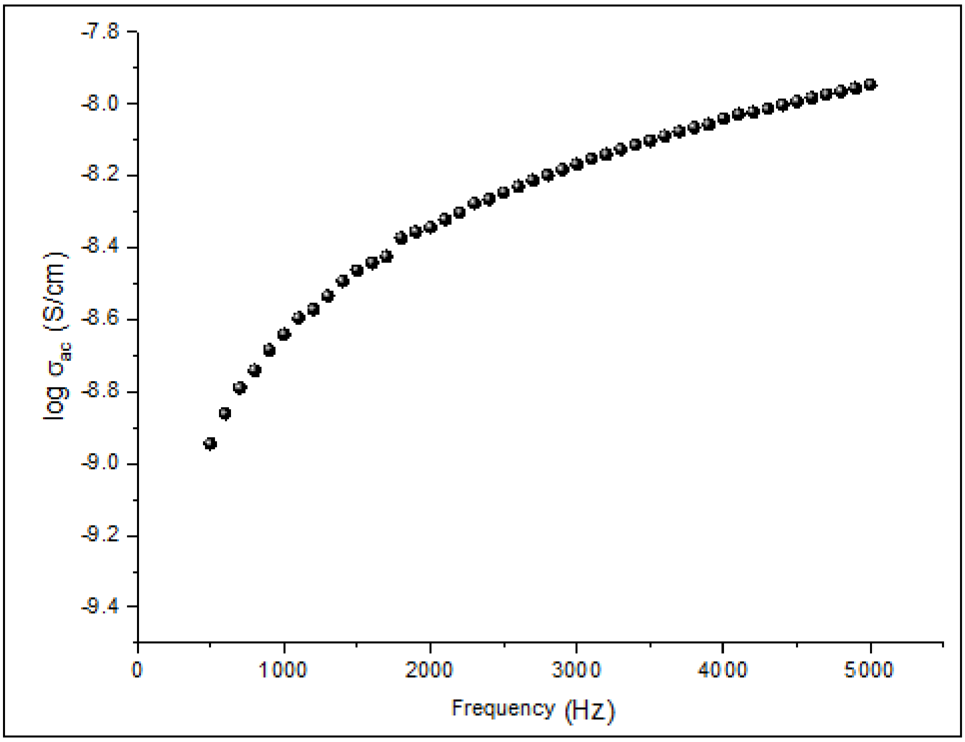


Figure 10: Change of logarithm of conductivity value with frequency.

Table 3: Dielectric values of the polymer at 1 kHz and room temperature.

	Dielectric constant	**Dielectric loss**	σ_{ac}	**Log** σ_{ac}
P(nBMA)	4.1113	2.6023	2.28133E^{-9}	-8.64181

It has been observed that the dielectric constant and dielectric loss factor of the polymer decrease with increasing frequency. The dielectric constant and dielectric loss factor tend to decrease noticeably in the low frequency range. As high frequency values are approached, the tendency of the dielectric constant decreases, but the decrease continues, albeit slightly. The reason for the sudden decreases in the low frequency regions is that the charged dipoles in the polymer have a higher tendency to move in the direction of their own field than in the direction of the applied electric field in this frequency region [27]. It has been observed that the logarithm of the conductivity value of the polymer increases with increasing frequency. Since the conductivity values are less than 10^{-06}, we can say that these polymers exhibit insulating properties.

3.4. Biological Results

In the study, the antimicrobial activity of the synthesized polymer on five different microorganisms was investigated. Antimicrobial effects were measured as a function of the inhibition zone diameter (mm) in Table 4, DMSO was used as a negative control and compared with Clindamycin antibiotic disk.

Table 4: Antimicrobial effects of the polymer on 5 different microorganism strains (Zone diameters in mm)

	E.coli				*B. megaterium*				*S. aureus*				*C.albicans*				*K. pneumoniae*			
	125 µM	**250 µM**	**500 µM**	**1000 µM**	**125 µM**	**250 µM**	**500 µM**	**1000 µM**	**125 µM**	**250 µM**	**500 µM**	**1000 µM**	**125 µM**	**250 µM**	**500 µM**	**1000 µM**	**125 µM**	**250 µM**	**500 µM**	**1000 µM**
P(nBMA)	11±0,2	11±0,2	11±0,2	12±0,7	11±1,5	12±0,5	13±0,5	14±1,5	12±0,7	12±0,7	13±0,2	14±1,2	14±1,5	13±0,5	11±1,5	12±0,5	13±1,2	14±0,2	15±0,7	15±0,7
Clindamycin	20±1,4				22±0,6				23±1,6				20±1,4				22±0,6			

According to the results shown in Fig. 11, the Polymer showed good scavenging activity with 94% DPPH scavenging activity at all concentrations. Based on these results, it was determined that the Polymer in general and the concentrations used had a significant effect on the DPPH scavenging activity.

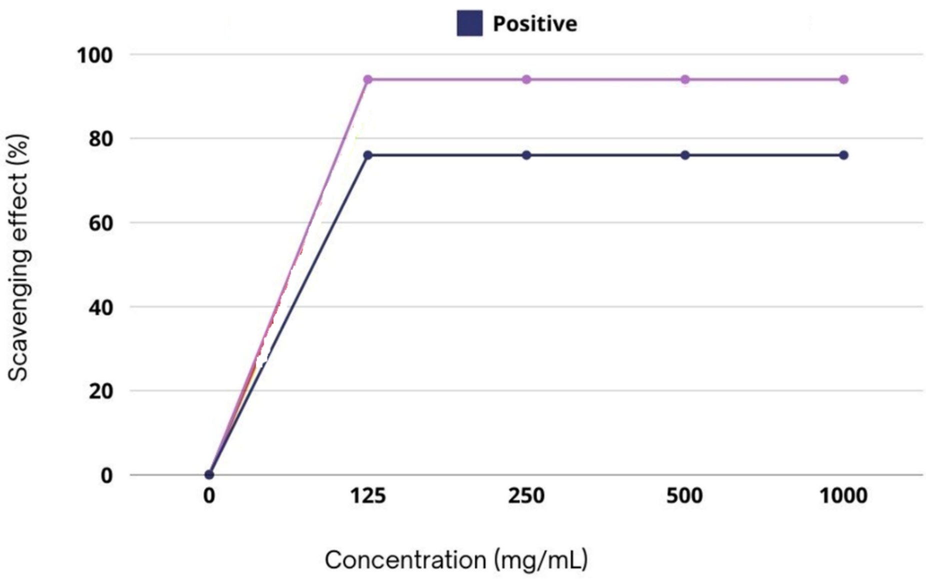


Figure 11: Percent inhibition of DPPH free radical scavenging activity of the polymer.

4. Conclusion

There are many methods for the synthesis of polymers. One of the most important of these methods is the ATRP method. The synthesis of new initiators that can be used in the ATRP method is very important for the scientific world. This study has proven that the initiator we synthesized can be used in the ATRP method. In this study, an initiator containing a chalcone group was synthesized in accordance with the literature. For this purpose, a benzofuran chalcone compound containing a hydroxy group was reacted with bromocetylbromide. The characterization of the synthesized compound was carried out by FT-IR and NMR spectrometers. Then, the synthesized initiator was polymerized with n-butyl methacrylate monomer. The ATRP method was used as the polymerization method. The average molecular weight and molecular weight distribution of the synthesized polymer were measured with a gel permeation chromatography (GPC) device at 25 °C using a refractive index (RI) detector at a solvent flow rate of 1 mL/min. Polystyrene was used as the standard substance and THF was used as the solvent. In the last stage, the dielectric and antimicrobial properties of the polymer were investigated. The Agar well method was used in the antimicrobial study. Dielectric properties were investigated as a function of frequency between 100 Hz and 5000 Hz at room temperature. In our study, it was determined that the polymer showed the best zone diameter (17 mm) against E. coli. When the antioxidant activity of the polymer was examined, it was seen that it had approximately 94% DPPH scavenging activity. In line with these results, it was determined that the polymer and the concentrations used had a significant effect on the DPPH scavenging activity. When the dielectric properties of the polymer were examined, it was observed that the dielectric constant and dielectric loss factor generally decreased with increasing frequency. It remained almost constant at high frequency values. When the conductivity value was examined, it was seen that the synthesized polymer had insulating properties.

Acknowledgements

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References

[1] Saçak, M., *Polymer Chemistry*, Gazi Bookstore, Ankara, Turkey, 2004.

[2] Köroğlu, A.M., *Synthesis, characterization and copolymerization of new methacrylate monomers and polymers carrying oxime esters in the minor branch*, Afyon Kocatepe University, Master Thesis, Afyon, 2006.

[3] Opletalova, V., Hartl, J., Palat, K.Jr., Patel, A., *Conformational analysis of 2-hydroxy-2',5'-diazachalcones*, Journal of Pharmaceutical and Biomedical Analysis, 23, 55–59, 2020.

[4] Indira, J., Karat, P.P., Sarojini, B.K., *Growth, characterization, and nonlinear optical property of chalcone derivative*, Journal of Crystal Growth, 242, 209–214. 2002.

[5] He, Z., Li, D., Hensley, D.K., Rondione, A.J., Chen, J., *Switching phase separation mode by varying the hydrophobicity of polymer additives in solution-processed semiconducting small-molecule/polymer blends*, Applied Physics Letters, 103, 113301, 2013.

[6] He, Z., Chen, J., Keum, J.K., Szulczewski, G., Li, D., *Improving performance of TIPS pentacene-based organic thin film transistors with small-molecule additives*, Org Electron 15, 150–155, 2014.

[7] Şentürk, A., *The Synthesis and Characterization of Methacrylate Polymers Bearing Chalcone*, Master's Thesis, Firat University, Elazig, Turkey, 2011.

[8] Ekbote, A.N., Maidur, S.R., Jahagirdar, J.R., Patil, P.S., Soma, V.R., *Femtosecond nonlinear optical investigations of nitro chalcones-doped PMMA thin films for optical limiting and photonic applications*, Materials Today Communications, 37, 107240, 2023.

[9] Fang, X., Yang, B., Cheng, Z., Zhang, P., Yang, M., *Synthesis and antimicrobial activity of novel chalcone derivatives,* Research on Chemical Intermediates, 40, 1715–1725, 2014.

[10] Sudhakar, C., Suresh, J., Valarmathi, N., Sumathi, S., Karthikeyan, A., et al., *Synthesis, characterization of acrylate polymer having chalcone moiety: evaluation of antimicrobial, anticancer and drug release study*, Journal Of Biomaterials Science-Polymer Edition, 32(4), 438–453, 2020.

[11] Bonesi, M., Loizzo, M.R., Statti, G.A., Michel, S., Tillequin, F., Menichini, F., *The synthesis and Angiotensin Converting Enzyme (ACE) inhibitory activity of chalcones and their pyrazole derivatives*, Bioorganic & Medicinal Chemistry Letters, 20(6), 1990–1993, 2010.

[12] Burmaoglu, S., Algul, O., Anıl, D.A., Gobek, A., Duran, G.G., Ersan, R.H., et al., *Synthesis and anti-proliferative activity of fluoro-substituted chalcones*, Bioorganic & Medicinal Chemistry Letters, 26(13), 3172–3176, 2016.

[13] Shenvi, S., Kumar, K., Hatti, K.S., Rijesh, K., Diwakar, L., Reddy, G.C., *Synthesis, anticancer and antioxidant activities of 2,4,5-trimethoxy chalcones and analogues from asaronaldehyde: Structure-activity relationship,* European Journal of Medicinal Chemistry, 62, 435–442, 2013.

[14] Hsieh, C.T., Hsieh, T.J., El-Shazly, M., Chuang, D.W., Tsai, Y.H., Yen, C.T., et al., *Synthesis of chalcone derivatives as potential anti-diabetic agents*. Bioorganic & Medicinal Chemistry Letters, 22(12), 3912–3915, 2012.

[15] Iqbal, H., Prabhakar, V., Sangith, A., Chandrika, B., Balasubramanian, R., *Synthesis, anti-inflammatory and antioxidant activity of ring-A-monosubstituted chalcone derivatives*, Medicinal Chemistry Research, 23, 4383–4394, 2014.

[16] Sashidhara, K.V., Avula, S.R., Mishra, V., Palnati, G.R., Singh, L.R., Singh, N., Chhonker, et al., *Identification of quinoline-chalcone hybrids as potential antiulcer agents*, European journal of medicinal chemistry, 89, 638–653, 2015.

[17] Pingaew, R., Saekee, A., Mandi, P., Nantasenamat, C., Prachayasittikul, S., Ruchirawat, S., et al., *Synthesis, biological evaluation and molecular docking of novel chalcone–coumarin hybrids as anticancer and antimalarial agents*, European Journal of Medicinal Chemistry, 85, 65–76, 2014.

[18] Shi, F., Fang, H., Xu, W., *Design, synthesis and biological activity of novel chalcone derivatives as anti-influenza agents,* Chemical Research in Chinese Universities, 32(1), 28–34, 2016.

[19] Mahapatra, D., Asati, V., Bharti, S.K., *Recent therapeutic progress of chalcone scaffold bearing compounds as prospective anti-gout candidates,* Journal of Critical Reviews, 6(1), 1–5, 2019.

[20] Demirelli, K., Kaya, E., Coşkun, M., Bagci, E., *Thermal degradation of two different polymers bearing amide pendant groups prepared by ATRP method*, Journal of Thermal Analysis and Calorimetry, 114(2), 917–926, 2013.

[21] Jobish, J., Charoen, N., Praveen, P., *Dielectric properties and AC conductivity studies of novel NR/PVA full-interpenetrating polymer networks*, Journal of Non-Crystalline Solids, 358(8), 1113–1119, 2012.

[22] Kamath, A., Devendrappa, H., *Concentration-dependent ionic conductivity and dielectric relaxation of methyl blue-dyed polyethylene oxide films*, Polymer Bulletin, 72(10), 2705–2724, 2015.

[23] Coşkun D., *The Synthesis of Benzofurane Substituted α,β-Unsaturated Ketones and Their Derivatives*, PhD Thesis, Firat University, Elazig, Turkey, 2008.

[24] Arslan Ateşşahin, D., Kadioğlu Dalkiliç, L., Özeren, Y., Dalkiliç, S., Çakmak, K., et al., *Investigation of Cytotoxic, Antimicrobial and Antioxidant Activity of Echium vulgare L. Seed*, International Journal of Nature and Life Sciences, 7(2), 129–135, 2023.

[25] Dalkılıç, S., Kadıoğlu Dalkılıç, L., Korkmaz, İ., *Antimicrobial Effect of Traditional Breakfast Zahter*, Gumuşhane University Science Institute Journal, 10(1), 128–133, 2020.

[26] Baliyan, S., Mukherjee, R., Priyadarshini, A., Vibhuti, A., Gupta, A., Pandey, R. P., et al., *Determination of Antioxidants by DPPH Radical Scavenging Activity and Quantitative Phytochemical Analysis of Ficus religiosa*, Molecules, 27(4), 1326, 2022.

[27] Çavuş, M.S., *Defect-Assisted Fractional Stochastic Ising Model of Dielectric Relaxation*, Çukurova University, PhD Thesis, Adana, 2010.