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# Investigation of the Thermal, Kinetic, and Dielectric Properties of a Novel Methacrylate Polymer Derived from Naphthol-Containing Cinnamic Acid Derivative

**Eray ÇALIŞKAN[1*], Kenan KORAN[2], Fatih BİRYAN[2]**

[1] Bingol University, Faculty of Science and Arts, Chemistry Department, Bingöl, Türkiye
[2] Fırat University, Faculty of Science, Chemistry Department, Elazığ, Türkiye
Eray ÇALIŞKAN ORCID No: 0000-0003-2399-4100
Kenan KORAN ORCID No: 0000-0002-2218-7211
Fatih BİRYAN ORCID No: 0000-0001-9198-3329

*Corresponding author: ecaliskan@bingol.edu.tr*

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Polymer, Dielectric, Thermal stability, Cinnamic acid

**Abstract:** The study investigates the thermal, kinetic, and dielectric properties of a novel methacrylate polymer synthesized from a naphthol-containing cinnamic acid derivative. Notably, the glass transition temperature (Tg) of the polymer, a crucial parameter for amorphous polymers, was found to be significantly higher than traditional methacrylate polymers, owing to the presence of the naphthol group within the polymer structure. The research also delves into the thermal stability and activation energy of the polymer using thermal analysis techniques. Additionally, the dielectric properties of the homopolymer were explored with a focus on the temperature-dependent changes in the dielectric constant and its behavior with varying frequencies.



# Naftol İçeren Sinnamik Asit Türevinden Türetilen Yeni Bir Metakrilat Polimerinin Termal, Kinetik ve Dielektrik Özelliklerinin İncelenmesi

**Anahtar Kelimeler**
Polimer, Dielektrik, Termal kararlılık Sinnamik asit

**Öz:** Bu çalışmada, naftol içeren bir sinnamik asit türevinden sentezlenen yeni bir metakrilat polimerinin termal, kinetik ve dielektrik özellikleri incelenmiştir. Özellikle, amorf polimerler için çok önemli bir parametre olan polimerin camsı geçiş sıcaklığının (Tg), polimer yapısındaki naftol grubunun varlığı nedeniyle geleneksel metakrilat polimerlerinden önemli ölçüde daha yüksek olduğu bulunmuştur. Araştırmada ayrıca termal analiz teknikleri kullanılarak polimerin termal kararlılığı ve aktivasyon enerjisi de incelenmiştir. Ek olarak, homopolimerin dielektrik özellikleri, dielektrik sabitindeki sıcaklığa bağlı değişikliklere ve değişen frekanslardaki davranışına odaklanılarak araştırılmıştır. Bu çalışma, naftol içeren bir sinnamik asit türevinden sentezlenen yeni bir metakrilat polimerinin termal, kinetik ve dielektrik özelliklerini araştırmaktadır. Özellikle, amorf polimerler için çok önemli bir parametre olan polimerin camsı geçiş sıcaklığının (Tg), polimer yapısındaki naftol grubunun varlığı nedeniyle geleneksel metakrilat polimerlerinden önemli ölçüde daha yüksek olduğu bulunmuştur. Araştırmada ayrıca termal analiz teknikleri kullanılarak polimerin termal kararlılığı ve aktivasyon enerjisi de incelenmiştir. Ek olarak, homopolimerin dielektrik özellikleri, dielektrik sabitindeki sıcaklığa bağlı değişikliklere ve değişen frekanslardaki davranışına odaklanılarak araştırılmıştır.

## 1. INTRODUCTION

Methacrylate polymer derivatives are a group of polymers that are derived from methacrylate monomers but have been modified or functionalized to exhibit specific properties or applications[1-3]. These derivatives can have a wide range of physical properties and applications, depending on the nature of the modifications. Methacrylate polymers can be functionalized with various groups or additives to impart specific properties, such as conductivity, flame resistance, or antimicrobial properties. These functional polymers have applications in electronics, textiles, and healthcare [4, 5].

The electrical and thermal behavior of polymers with methacrylate main chains has been the subject of extensive study, owing to their diverse application [6-8]. With a well-established understanding of the degradation mechanisms inherent to methacrylate polymers, various investigations have delved into elucidating rate constants and activation energy values associated with their thermal degradation. The thermal stability of polymers is of paramount significance due to its critical role in numerous applications. In recent years, the research landscape has expanded to encompass studies concerning the thermal degradation of methacrylate and acrylate main chain polymers bearing distinctly different side groups, further enhancing our understanding of these materials [9-13].

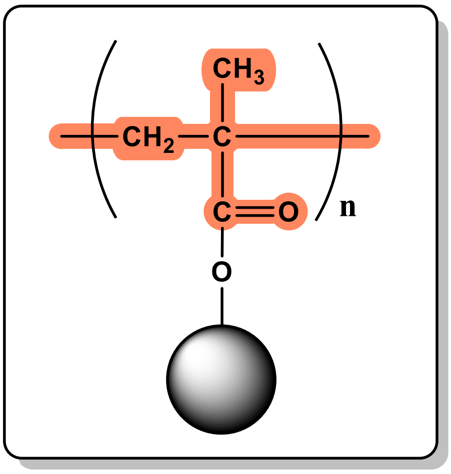


**Figure 1.** The general structure representation of modified methacrylate polymer

In this study, we synthesized a homopolymer utilizing a monomer derived from a naphthol-containing cinnamic acid derivative and methacryloyl chloride through free radical polymerization techniques. The resulting polymer was characterized extensively to explore its thermal, kinetic, and dielectric properties. Comparative analyses were conducted with existing literature data to gain insights into the unique behavior and performance of this novel polymer. Our findings provide valuable contributions to the evolving knowledge of methacrylate-based polymers and offer potential avenues for their enhanced utilization in various technological applications.

## 2. MATERIAL AND METHOD

This section begins with an overview of the four synthesis steps employed to create the polymer: the synthesis of naphthyl acrylic acid, attachment of a linker (4-amino phenol), and formation of the monomer using methacryloyl chloride. The use of free radical polymerization with AIBN as the initiator is explained. It also details the physical measurements performed, such as thermal analysis, determination of the activation energy, and dielectric properties analysis.

### 2.1. Synthesis

#### 2.1.1. General synthesis for compounds

The synthesis started with the reaction of malonic acid and naphthaldehyde under basic conditions to obtain a cinnamic acid derivative. Then, 4-amino phenol was used as a linker before the monomer step. After having (*E*)-N-(4-hydroxyphenyl)-3-(naphthalene-1-yl)acrylamide, the free radical polymerization method was preferred due to the suitability of the monomer.

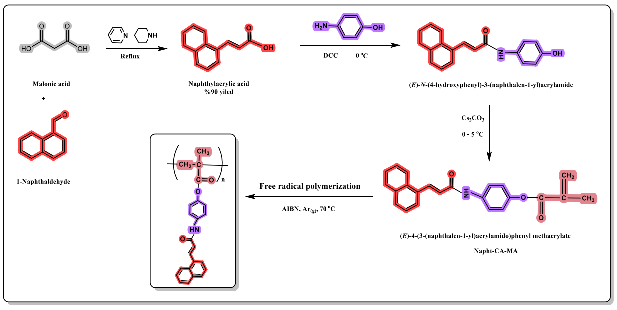


**Figure 2.** General synthesis steps for homopolymer

Free radical polymerization method was used for the polymerization of the monomer in the presence of a radical initiator (AIBN). Then, it was passed through argon gas and kept in an Oil Bath at 70 °C for 24 hours. Then obtained crude product was precipitated in ethanol and filtered. Obtained solid was dried under vacuum and characterized via spectroscopic methods.

### 2.2. Characterization of Compounds

#### 2.2.1. Characterizaiton of napthol-cinnamic acid

$^{1}H$ NMR (400 MHz, DMSO-$d_6$) δ 12.49 (s, 1H), 8.40 (d, *J* = 15.7 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 8.08 – 7.87 (m, 3H), 7.70 – 7.49 (m, 3H), 6.61 (d, *J* = 15.8 Hz, 1H). $^{13}C$ NMR (101 MHz, DMSO) δ 122.40, 123.45, 125.70, 126.20, 126.77, 127.62, 129.20, 130.85, 131.22, 131.46, 133.77, 140.64, 167.90.



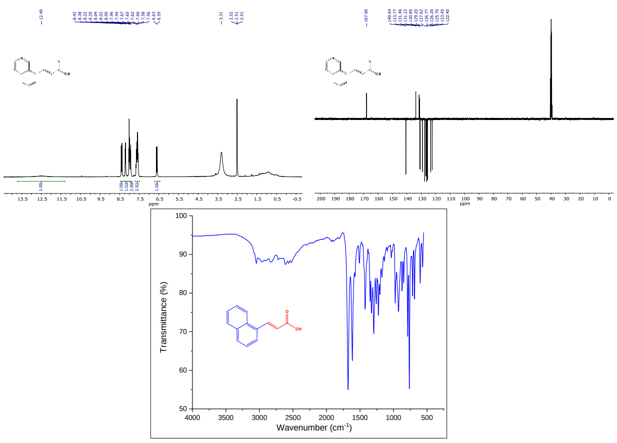


**Figure 3.** $^{1}H$, $^{13}C$ and FT-IR spectra of cinnamic acid compound

#### 2.2.2. Characterization of intermediate compound

$^{1}H$ NMR (400 MHz, DMSO-$d_6$) δ 10.06 (s, 1H), 9.26 (s, 1H), 8.33 (d, *J* = 15.5 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 7.3 Hz, 1H), 7.62 (dt, *J* = 15.2, 7.8 Hz, 3H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 15.4 Hz, 1H), 6.81 – 6.73 (m, 2H). $^{13}C$ NMR (101 MHz, DMSO) δ 39.72, 115.46, 115.70, 120.71, 121.51, 123.04, 123.71, 125.08, 126.08, 126.24, 126.74, 127.43, 129.16, 130.16, 136.37, 154.05, 163.33.

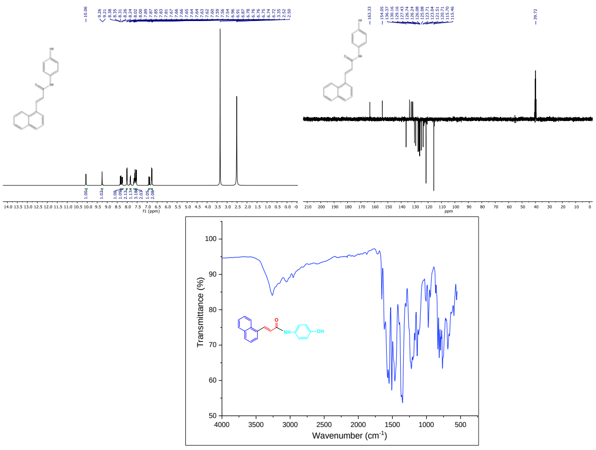

**Figure 4.** $^{1}$H, $^{13}$C and FT-IR spectra of intermediate compound

### 2.2.3. Characterization of monomer

$^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 10.40 (d, $J$ = 9.1 Hz, 1H), 8.61 – 8.18 (m, 4H), 8.02 (dd, $J$ = 8.1, 3.7 Hz, 4H), 7.93 – 7.71 (m, 5H), 7.61 (tt, $J$ = 21.6, 19.3, 6.9 Hz, 6H), 7.36 – 7.09 (m, 3H), 7.05 – 6.72 (m, 2H), 6.30 (d, $J$ = 4.6 Hz, 1H), 5.90 (s, 1H), 2.03 (d, $J$ = 4.6 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 39.72, 115.46, 115.70, 120.71, 121.51, 123.04, 123.71, 125.08, 126.08, 126.24, 126.74, 127.43, 129.16, 130.16, 136.37, 154.05, 163.33.

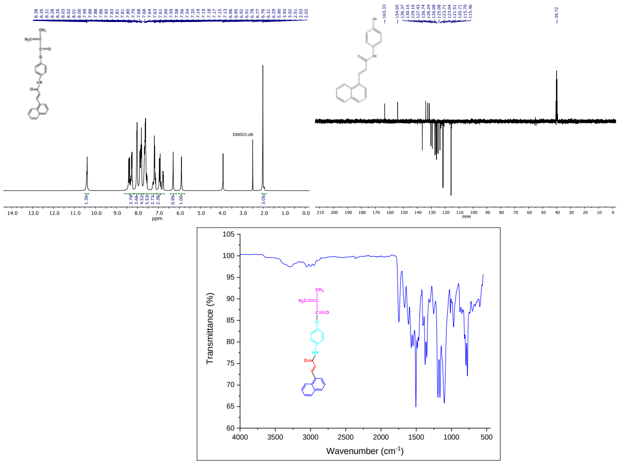

**Figure 5.** $^{1}$H, $^{13}$C and FT-IR spectra of monomer

### 2.2.4. Characterization of polymer compound

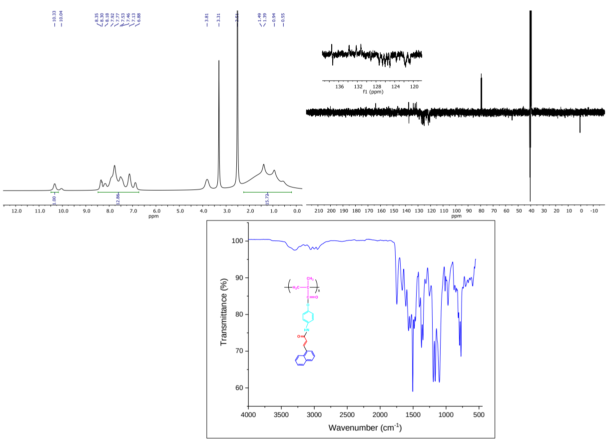

**Figure 6.** $^{1}$H, $^{13}$C and FT-IR spectra of polymer compound

### 2.3. Physical Measurements

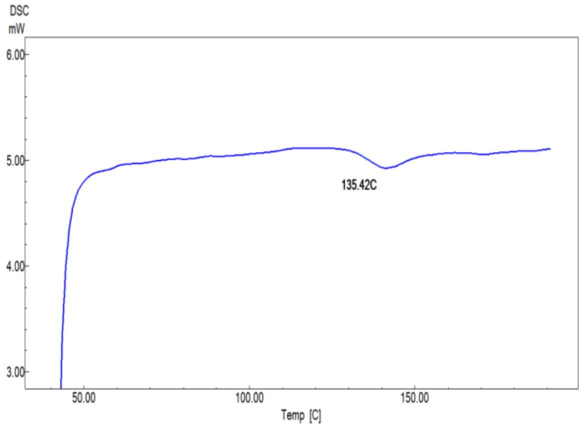


**Figure 7.** The glass transition temperature of polymer

DSC analysis was performed under a nitrogen atmosphere from ambient temperature to 200 °C at a heating rate of 20 °C min$^{-1}$. The glass transition temperature was determined as 135.42 °C. This temperature is considerably higher than some methacrylate polymers in the literature. This is thought to be due to the presence of the naphthol group, which is a hard and bulky structure, in the side chain of the homopolymer. The glass transition temperature of amorphous polymers is related to the chain flexibility. Napthol group in the structure of polymer decreases chain flexibility and increase Tg.

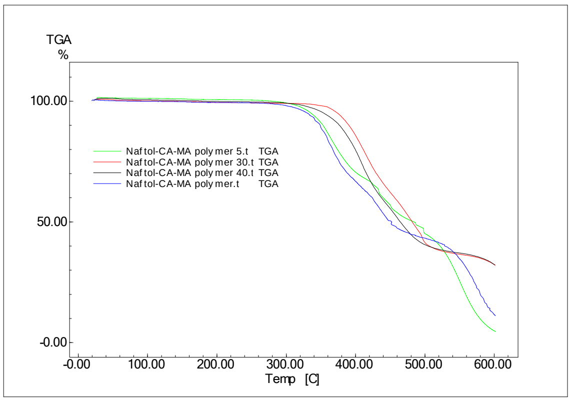


**Figure 8.** TGA analysis of polymer

In order to determine the thermal stability of the naphthol polymer, TGA analyses were performed in an argon atmosphere. The decomposition temperature was determined as 332 ºC in the analysis performed at a heating rate of ºC min$^{-1}$.

Thermal degradation activation energy values were calculated from TGA analysis of the polymer at different heating rates. The activation energies calculated according to the conversion percentages in the range of 2% to 35% were determined in the range of 115.37-187.18 kJ mol$^{-1}$. The average activation energy was calculated as 139.22 kJ mol$^{-1}$.

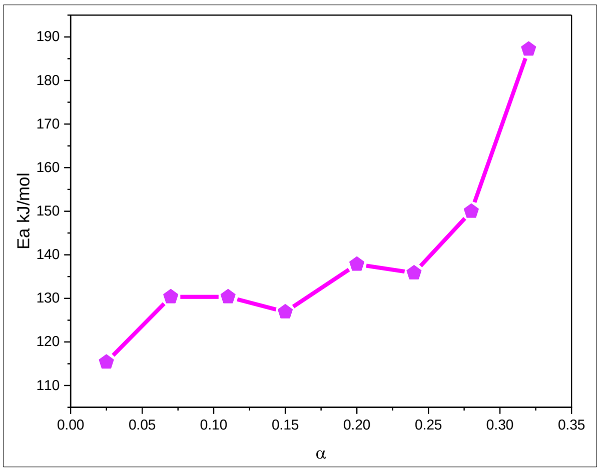


**Figure 9.** Activation energy graph of polymer

**Table 1.** Thermal properties of polymer different heating rates

| Sample | T $_{initial}$ ($^{O}$C) | Residue at 400 $^{O}$C | Residue at 600 $^{O}$C |
|---|---|---|---|
| **5 $^{O}$C/min** | 332 | 66 | 4 |
| **10 $^{O}$C/min** | 338 | 70 | 11 |
| **30 $^{O}$C/min** | 356 | 81 | 31 |
| **40 $^{O}$C/min** | 367 | 87 | 31 |

**Table 2.** Dielectric parameters of samples at 1 kHz at various temperature

| Sample | Dielectric constant | AC conductivity (S/cm) | Log $\sigma_{ac}$ |
|---|---|---|---|
| **273K** | 8.47 | $2.55x10^{-10}$ | -9.593 |
| **300K** | 10.80 | $1.03x10^{-08}$ | -7.731 |
| **320K** | 10.83 | $1.86x10^{-08}$ | -7.524 |
| **355K** | 13.44 | $9.57x10^{-07}$ | -6.018 |

Dielectric behaviors of homopolymer were performed as a function of frequency in the 100 Hz to 70 kHz range. The dielectric constant decreases with increasing frequency. Dipole movements are constrained and the polarization effect is diminished in a stronger electric field. The ac conductivity values for alternating current are also in a similar state. A significant change was observed in the dielectric constant of the polymer with the increase in temperature. The dielectric constant increased from 8.47 to 13.44 at 1 kHz from room temperature to 355K.

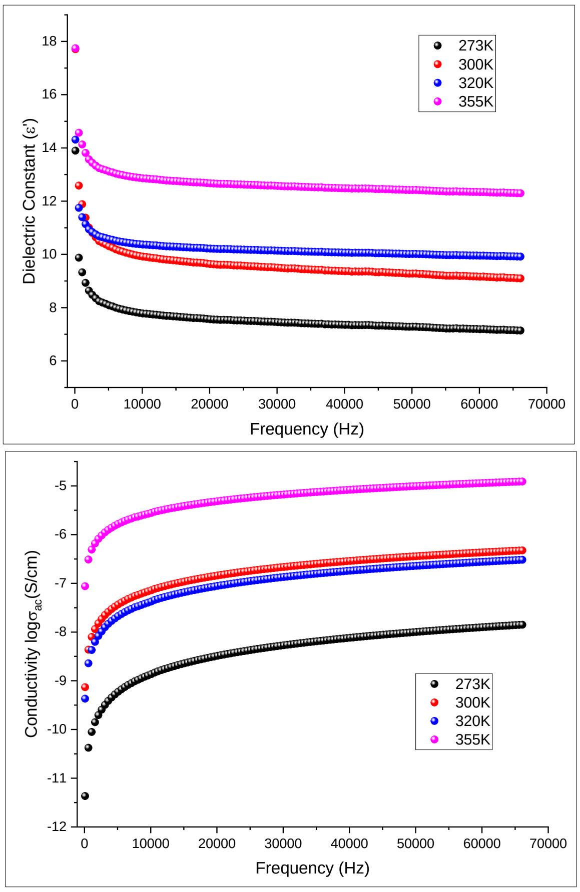


**Figure 10.** Dielectric properties of polymer

## 3. RESULTS

The results indicates that the polymer's glass transition temperature (Tg), measured at 135.42 °C. The significantly higher Tg, compared to other methacrylate polymers, is attributed to the presence of the naphthol group in the polymer's side chain, which reduces chain flexibility and increases Tg. Additionally, the thermal stability of the polymer, as determined by TGA analysis, revealed a decomposition temperature of 332 °C. The activation energy values calculated from TGA analysis at different heating rates were in the range of 115.37-187.18 kJ $mol^{-1}$, with an average activation energy of 139.22 kJ $mol^{-1}$. Furthermore, the dielectric behavior of the homopolymer was discussed, focusing on how the dielectric constant changes with increasing frequency and temperature.

## 4. DISCUSSION AND CONCLUSION

In this section, the results are interpreted and their implications are explained. The significance of the higher Tg, linked to the presence of the naphthol group, is discussed in terms of chain flexibility. The impact of the novel polymer's properties on potential applications is explored, and the practical relevance of these findings is emphasized.

Methacrylate polymers containing cinnamic acid derivative are a type of polymers that incorporate cinnamic acid or its derivatives into the polymer backbone or side chains. These polymers can exhibit improved thermal stability, optical properties, shape-memory behavior, and biocompatibility[14, 15]. Several examples are given below;

Poly(phenyl cinnamate-co-methyl methacrylate) (PPCM), a copolymer of phenyl cinnamate and methyl methacrylate, which can form liquid crystalline phases and exhibit photoresponsive behavior. Poly(4-hydroxycinnamoyl methacrylate) (PHCMA), a homopolymer of 4-hydroxycinnamoyl methacrylate, which can undergo reversible crosslinking and de-crosslinking upon exposure to UV light and heat, respectively. Poly(3,4-dihydroxycinnamoyl methacrylate) (PDHCMA), a homopolymer of 3,4-dihydroxycinnamoyl methacrylate, which can form hydrogen-bonded supramolecular networks and exhibit shape-memory and self-healing properties. Poly(3,4-dihydroxycinnamoyl methacrylate-co-methyl methacrylate) (PDHCMA-MMA), a copolymer of 3,4-dihydroxycinnamoyl methacrylate and methyl methacrylate, which can show enhanced mechanical strength and thermal stability compared to PDHCMA. Poly(3,4-dihydroxycinnamoyl methacrylate-co-ethylene glycol dimethacrylate) (PDHCMA-EGDMA), a crosslinked copolymer of 3,4-dihydroxycinnamoyl methacrylate and ethylene glycol dimethacrylate, which can display shape-memory and self-healing properties as well as biodegradability.

In summary, methacrylate polymer derivatives are versatile materials with a broad range of physical properties and applications. Their tunable characteristics make them valuable in various industries, from optics and automotive to healthcare and electronics. We have developed a novel homopolymer by using a cinnamic acid derivative and conducted several physical experiments in order to understand the thermal and dielectric characteristics of the polymer. The results demonstrated potential physical properties, especially, the dielectric constant is considerably high value compared to similar structures in literature. Academic research in this field continually explores new derivatives and applications to meet evolving industrial needs.

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