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Structural and chromatographic characterization of acrylate-urethane hybrid copolymers synthesized via two-step polymerization

Bakhtiyor Qudratovich Shaykulov

baxtiyor_sh@bk.ru

Tashkent research institute of chemical technology

Research Article

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Abstract

This study investigates the synthesis of a novel acrylate-urethane hybrid copolymer through a systematic two-step functionalization method. The effect of reaction temperature on the yield was evaluated, identifying an optimal temperature range of 70–75°C, which resulted in a maximum conversion of 85–90%. The chemical architecture of the copolymer was rigorously characterized using Fourier-transform infrared (FTIR) and multi-dimensional Nuclear Magnetic Resonance (^{13} C, DEPT-135) spectroscopy. Spectral analysis confirmed the covalent integration of acrylate (δ 174.5 ppm) and urethane (δ 155.8 ppm) moieties, verifying the complete consumption of isocyanate groups. Gel permeation chromatography (GPC) revealed a monomodal distribution with a weight-average molecular weight (M_w) of 7.1 kDa and a polydispersity index (PDI) of 1.77. These results demonstrate that the synthesized hybrid copolymer is a promising candidate for high-performance protective coatings with high macromolecular homogeneity.

1. Introduction

The development of hybrid polymer systems has emerged as a transformative approach in material science, aiming to synergize the distinct advantages of disparate polymer classes [1, 2]. Among these, acrylate-urethane hybrid copolymers have garnered significant attention due to their ability to combine the superior weathering resistance, optical clarity, and cost-effectiveness of polyacrylates with the exceptional mechanical toughness, abrasion resistance, and flexibility characteristic of polyurethanes [3]. Unlike simple physical blends, which often suffer from macro-phase separation and poor long-term stability, chemically integrated hybrid copolymers offer enhanced interfacial adhesion and macromolecular homogeneity [4, 5].

In recent years, the demand for high-performance protective coatings in the automotive, aerospace, and textile industries has driven the search for more efficient synthesis routes [6]. Traditional polyurethane-acrylate (PUA) synthesis often involves complex multi-stage processes or the use of hazardous solvents. The challenge remains in achieving precise control over the molecular weight distribution and the degree of functionalization while maintaining high conversion rates [7]. The integration of acrylate moieties into the urethane backbone through a controlled two-step polymerization process presents a viable solution to these challenges, allowing for the tailoring of the final polymer’s thermo-mechanical properties [8, 9].

Despite the extensive research in this field, detailed chromatographic and structural characterization of the intermediate and final hybrid architectures is often underreported. Understanding the relationship between reaction parameters, such as temperature and stoichiometry, and the resulting molecular weight distribution is crucial for industrial scalability and performance optimization [10].

This study focuses on the systematic synthesis of a novel acrylate-urethane hybrid copolymer via a two-step functionalization strategy. The primary objective is to evaluate the effect of reaction temperature on

the polymerization efficiency and to provide a comprehensive structural validation using Fourier-transform infrared (FTIR) and multi-dimensional Nuclear Magnetic Resonance (^{13} C and DEPT-135 NMR) spectroscopy [11, 12]. Furthermore, Gel Permeation Chromatography (GPC) was employed to assess the macromolecular uniformity and polydispersity of the synthesized system [10, 13]. The findings presented herein contribute to the fundamental understanding of hybrid formation and provide a robust framework for the design of next-generation protective coating materials.

2. Experimental section

2.1. Synthesis of acrylate-urethane copolymer.

The synthesis of the acrylate-urethane hybrid copolymer was executed via a controlled two-step functionalization strategy, governed by nucleophilic addition and subsequent polyaddition mechanisms. The process was performed in a multi-neck glass reactor equipped with a high-torque mechanical stirrer, a reflux condenser, and a precision digital thermostat.

In the first stage, stoichiometric amounts of isophorone diisocyanate (IPDI, supplied by Global Chemical) and the oligoester were introduced into the reactor. The mixture was dissolved in anhydrous dimethylformamide (DMF), which served as the reaction medium, and heated to 60–65°C to facilitate the formation of an isocyanate-terminated prepolymer.

In the second stage, calculated amounts of acrylic acid and dibutyltin dilaurate (DBTDL) as a specific urethane-forming catalyst (0.1 wt.%) were introduced. The reaction temperature was maintained within the optimized range of 70–75°C to ensure high conversion efficiency. The reaction progress was monitored via FTIR spectroscopy and continued until the characteristic absorption band of free isocyanate groups at 2270 cm^{-1} completely disappeared, signifying quantitative consumption. The resulting viscous solution was purified by double reprecipitation in cold diethyl ether to remove unreacted monomers and catalyst residues. Finally, the synthesized copolymer was dried in a vacuum oven at 40°C until a constant weight was achieved.

2.2. FTIR spectroscopic analysis.

The functional groups and chemical bonding of the synthesized hybrid copolymer were characterized using Fourier-transform infrared (FTIR) spectroscopy [14]. Spectra were recorded on a Shimadzu IR-Affinity-1S spectrometer in the wavenumber range of 4000–400 cm^{-1}. Samples were prepared using the attenuated total reflectance (ATR) technique. For each measurement, 32 scans were accumulated with a resolution of 4 cm^{-1} to ensure a high signal-to-noise ratio. All spectra were baseline-corrected and normalized to allow for accurate identification of characteristic absorption bands, such as urethane N–H, carbonyl C = O, and ether C–O–C groups. Data acquisition was performed using LabSolutions IR software (v.2.1, Shimadzu, Japan).

2.3. NMR spectroscopic measurements.

^{13} C and DEPT-135 NMR spectra were recorded on a JEOL JNM-ECZ600R spectrometer operating at a frequency of 600 MHz. The samples were prepared by dissolving the copolymer in a calibrated mixture of DMSO-d_6 and CCl_4 to achieve optimal signal resolution for both polar and non-polar segments. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal reference.

For ^{13} C NMR measurements, the following acquisition parameters were utilized: a spectral width of 31,000 Hz, a pulse delay (D1) of 2.0 s, and an accumulation of 10,000 scans. The DEPT-135 experiments were conducted using a 135° flip angle to distinguish between methine (CH), methylene (CH_2), and methyl (CH_3) carbon resonance signals. Data acquisition and post-experimental processing were performed using JEOL Delta software (v.5.3.1).

2.4. Molecular weight analysis.

The molecular weight distribution and average molecular weights (M_w, M_n) were determined using an Agilent 1260 Infinity II GPC/SEC system [15]. Tetrahydrofuran (THF) was employed as the mobile phase at a constant flow rate of 1.0 mL/min at 35°C. The elution profile was monitored using a refractive index detector (RID) over a total run time of 15 minutes. The system was calibrated using a series of narrow-distribution polystyrene standards (Agilent) with molecular weights ranging from 2 kDa to 100 kDa. Chromatographic data were processed using Agilent GPC/SEC Software to calculate the polydispersity index (PDI = M_w / M_n).

3. Results and discussion

3.1. Synthesis mechanism and technological factors.

In the first stage of the synthesis, the formation of the urethane chain occurs. Here, isocyanate groups (-NCO) and hydroxyl-containing components undergo a copolymerization reaction to form stable urethane bonds. In the second stage, the functionalization of the copolymer chain is achieved through the introduction of acrylic acid fragments. The carboxyl groups (-COOH) and unsaturated double bonds (C = C) in acrylic acid facilitate subsequent chemical modification and cross-linking of the synthesized product. This structure ensures that the sample possesses both elasticity (due to urethane blocks) and high adhesion and mechanical strength (due to acrylate blocks).

3.2. Effect of reaction temperature.

To determine the efficiency of the copolymerization process, the effect of temperature on the reaction yield was systematically analyzed (Fig. 1). It was found that the reaction yield increases sharply as the temperature rises from 40°C to 70°C. This is explained by the increase in the kinetic energy of the molecules in the system. However, a further increase in temperature (80°C and above) leads to a decrease in yield, which can be attributed t8o the acceleration of side destructive reactions at higher temperatures. The optimal temperature range was determined to be 70–75°C.

3.3. FTIR spectroscopic analysis.

The nature of the functional groups and chemical bonds of the synthesized acrylate-urethane copolymer was analyzed using FTIR spectroscopy (Fig. 2). The absorption bands in the spectrum confirm the presence of both urethane and acrylate fragments in the macromolecular chain.

The following characteristic absorption regions were identified:

3320–3450 cm^{-1}: A broad and intense peak corresponding to the stretching vibrations of the –NH– bond in the urethane group.

2850–2960 cm: Vibrations of –CH and –CH groups in the aliphatic chain.
1720–1735 cm^{-1}: The most intense peak, corresponding to the carbonyl (C = O) vibrations in both acrylate and urethane groups.

1530–1560 cm: Amide-II bands (–NH– deformation and C–N stretching) of the urethane fragment.

1150–1250 cm^{-1}: Stretching vibrations of the ester (C–O–C) bonds. Notably, no absorption band was observed at 2270 cm^{-1} (characteristic of free isocyanate groups), indicating that all initial -NCO groups reacted completely [6].

3.4. Characterization of copolymer structure using NMR spectroscopy

The detailed macromolecular architecture and chemical composition of the synthesized hybrid were rigorously elucidated using ^{13} C NMR and DEPT-135 spectroscopic techniques (Fig. 3). The resonance signals observed in the carbon spectra provide definitive evidence of the successful integration of both acrylate and urethane segments into the copolymeric backbone

Carbonyl and Urethane Regions (δ 155–180 ppm)

The carbonyl region exhibits distinct resonance signals that substantiate the hybrid nature of the system. The signals in the range of δ 170.5–175.8 ppm are attributed to the ester carbonyl carbons (C = O) belonging to the acrylate units. Concurrently, the signals appearing at δ 155.8 ppm correspond to the quaternary carbon atoms of the urethane (-NH-COO-) linkages, confirming the formation of the carbamate groups.

Aromatic and Aliphatic Regions

The aromatic carbon resonances located between δ 110 and 145 ppm represent the benzene ring carbons derived from the hard segments of the urethane component. In the aliphatic region (δ 20–70

ppm), signals corresponding to the methylene (-CH_2-) and methine (-CH-) groups of the polymer backbone were identified. Specifically, the resonance signals in the δ 60–68 ppm range are characteristic of carbon atoms adjacent to ether linkages

(-CH_2-O-), which confirms the covalent incorporation of the oligoester segments into the hybrid structure.

DEPT-135 Analysis

To further clarify the carbon hybridization states and their respective proton attachments, DEPT-135 experiments were compared with the standard ^{13} C NMR spectrum. This multi-dimensional approach enabled the clear differentiation between methyl (CH_3), methylene (CH_2), and methine (CH) groups. The DEPT-135 phase assignments (Table 1) provide a high-fidelity structural map, substantiating the theoretical synthesis mechanism through empirical spectral data.

Table 1

^{13}C NMR chemical shifts and DEPT-135 phase assignments

No.	Chemical shift (δ, ppm)	DEPT-135 phase	Assignment
1	174.5	Quaternary	C = O (Acrylate)
2	155.8	Quaternary	NH-COO (Urethane)
3	125.0–135.0	Positive	Ar-CH (Aromatic)
4	65.5	Positive/Negative	-CH_2-O- (Ester bond)
5	28.0–42.0	Positive/Negative	-CH_2-, -CH- (Chain)

3.5. Molecular weight characterization (GPC).

The average molecular weight distribution of the synthesized sample was investigated using Gel Permeation Chromatography (GPC) (Fig. 4). The obtained chromatogram spans an elution time from 5 to 15 minutes, with the primary high-intensity peak appearing in the high-molecular-weight fraction region.

According to the analytical results, the copolymer contains a negligible amount of low-molecular-weight (2–3 kDa) fractions, while the majority of the polymer chains are distributed in the region above 5 kDa. The monomodal nature (single peak) of the chromatographic curve confirms the formation of a single hybrid copolymer system rather than a physical blend of homopolymers. Furthermore, the low polydispersity index (PDI) indicates a high degree of control over the polymerization process and suggests a uniform growth of the macromolecular chains.

Table 2 Molecular weight characteristics of the synthesized acrylate-urethane copolymer

Sample	Peak time (min)	M_n (kDa)	M_w (kDa)	PDI (M_w/M_n)
Acrylate-urethane copolymer	5–15	~ 5.2	~ 7.1	1.77

Thus, the complex analysis of the copolymer using FTIR, NMR, and GPC methods confirms the formation of a well-defined acrylate-urethane hybrid structure with controlled molecular parameters.

4. Conclusion

The present study successfully established a robust methodology for the synthesis of a novel acrylate-urethane hybrid copolymer via a controlled two-step functionalization strategy. Systematic investigation of the process parameters and structural characteristics led to the following primary conclusions:

Process Optimization: The polymerization efficiency was found to be highly temperature-dependent, with an identified optimal range of 70–75°C. Within this thermal window, and through precise stoichiometric control of the isocyanate and hydroxyl components, a maximum chemical conversion of 85–90% was achieved.

Structural Integrity: Comprehensive FTIR spectroscopic analysis confirmed the successful formation of the target architecture. The total disappearance of the characteristic isocyanate absorption band at 2270 cm^{-1} verified the quantitative consumption of -NCO groups and the effective covalent integration of urethane and acrylate moieties.

Macromolecular Mapping: Advanced ^{13}C and DEPT-135 NMR studies provided definitive evidence of the hybrid skeleton. The distinct resonance signals at δ 155.8 ppm (urethane quaternary carbon) and δ 174.5 ppm (acrylate ester carbonyl) substantiated the distribution of functional segments within the polymer backbone.

Chromatographic Characterization: GPC analysis demonstrated high macromolecular homogeneity, evidenced by a monomodal elution profile. The synthesized system exhibited a weight-average molecular weight (M_w) of 7.1 kDa and a narrow polydispersity index (PDI = 1.77), indicating excellent control over the chain growth mechanisms.

In summary, the developed acrylate-urethane hybrid possesses a well-defined chemical structure and uniform molecular distribution. These attributes render the copolymer a highly promising candidate for the formulation of high-performance protective coatings, offering a synergistic balance of elasticity, adhesion, and mechanical durability for advanced industrial applications.

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Declarations

Author Contribution

1. Bakhtiyor Shaykulov PhD, Tashkent Research Institute of Chemical Technology ORCID: https://orcid.org/0009-0000-7695-46342. Dilafruz Gulboyeva PhD, Karshi State University 3. Fayzulla Nurkulov D.Sc., Prof., Tashkent Research Institute of Chemical Technology 4. Abdulahat Djalilov D.Sc., Prof., Academician, Tashkent Research Institute of Chemical Technology

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Figures

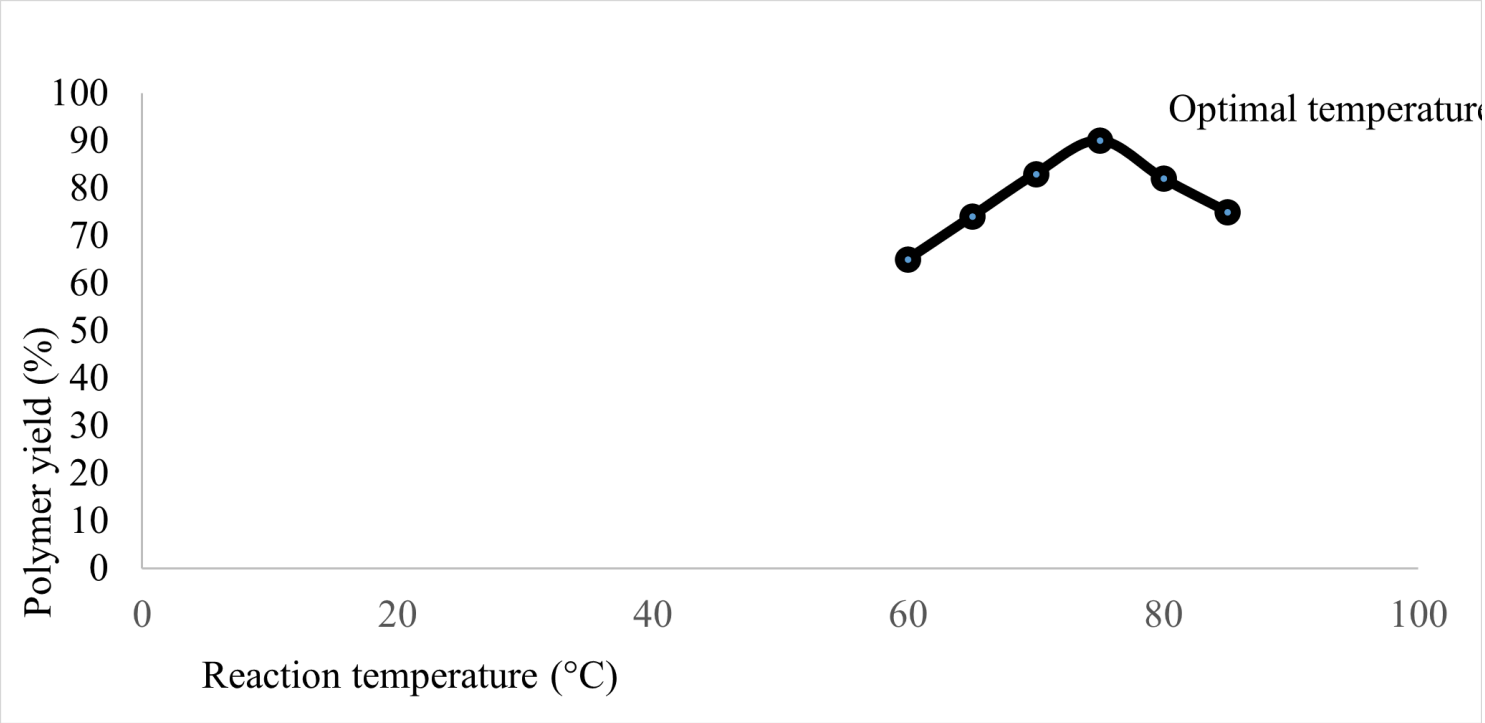


Figure 1

Dependence of polymer yield on the reaction temperature. The maximum yield was observed at 75°C.

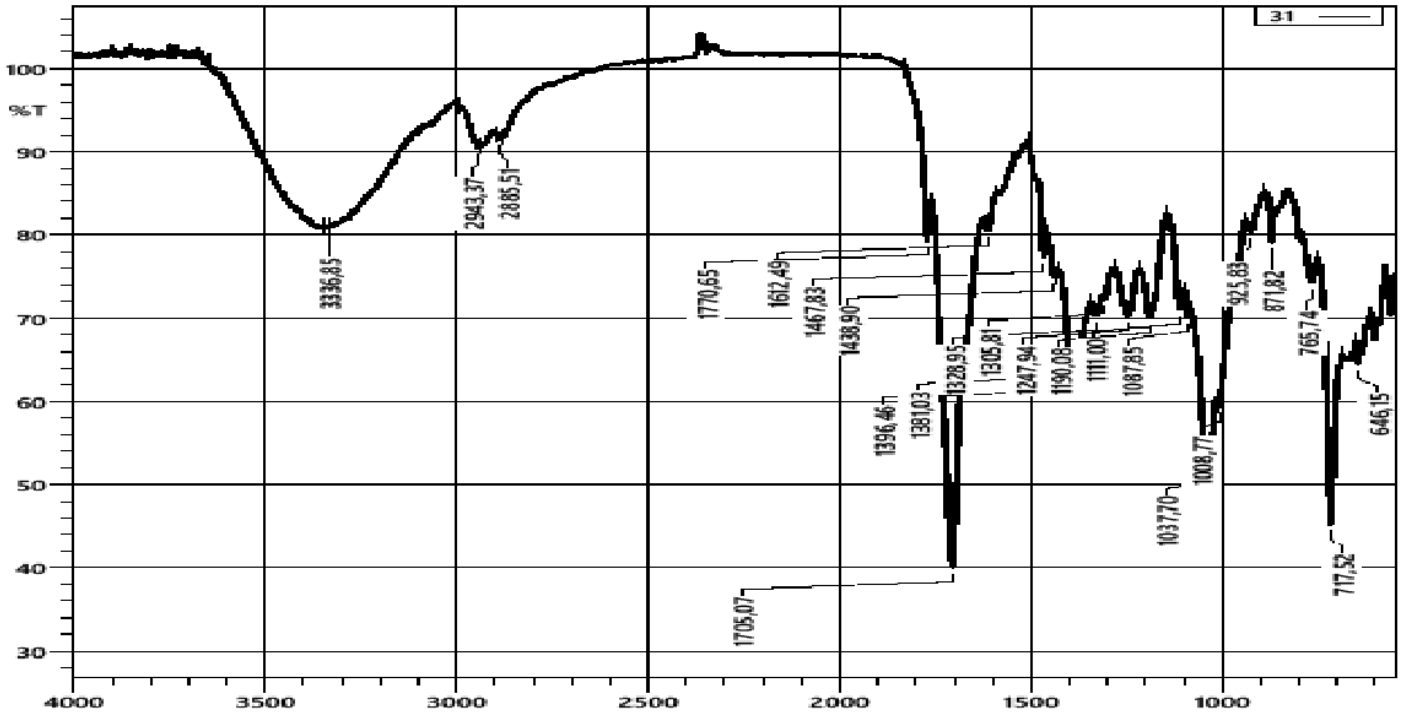


Figure 2

FTIR spectrum of the synthesized acrylate-urethane copolymer.

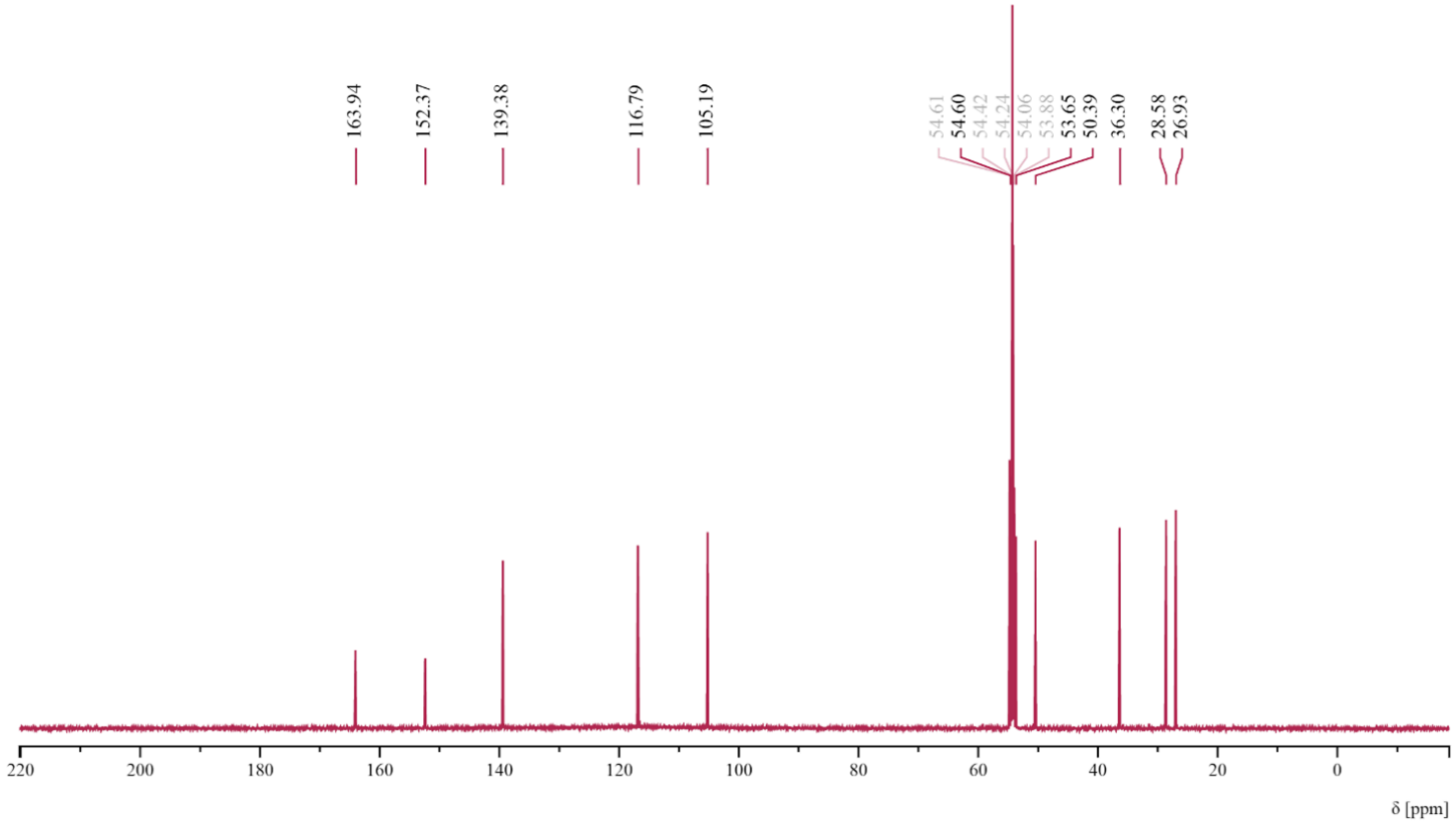


Figure 3

^{13}C NMR spectrum of the synthesized acrylate-urethane copolymer (600 MHz, DMSO-d_6/CCl_4).

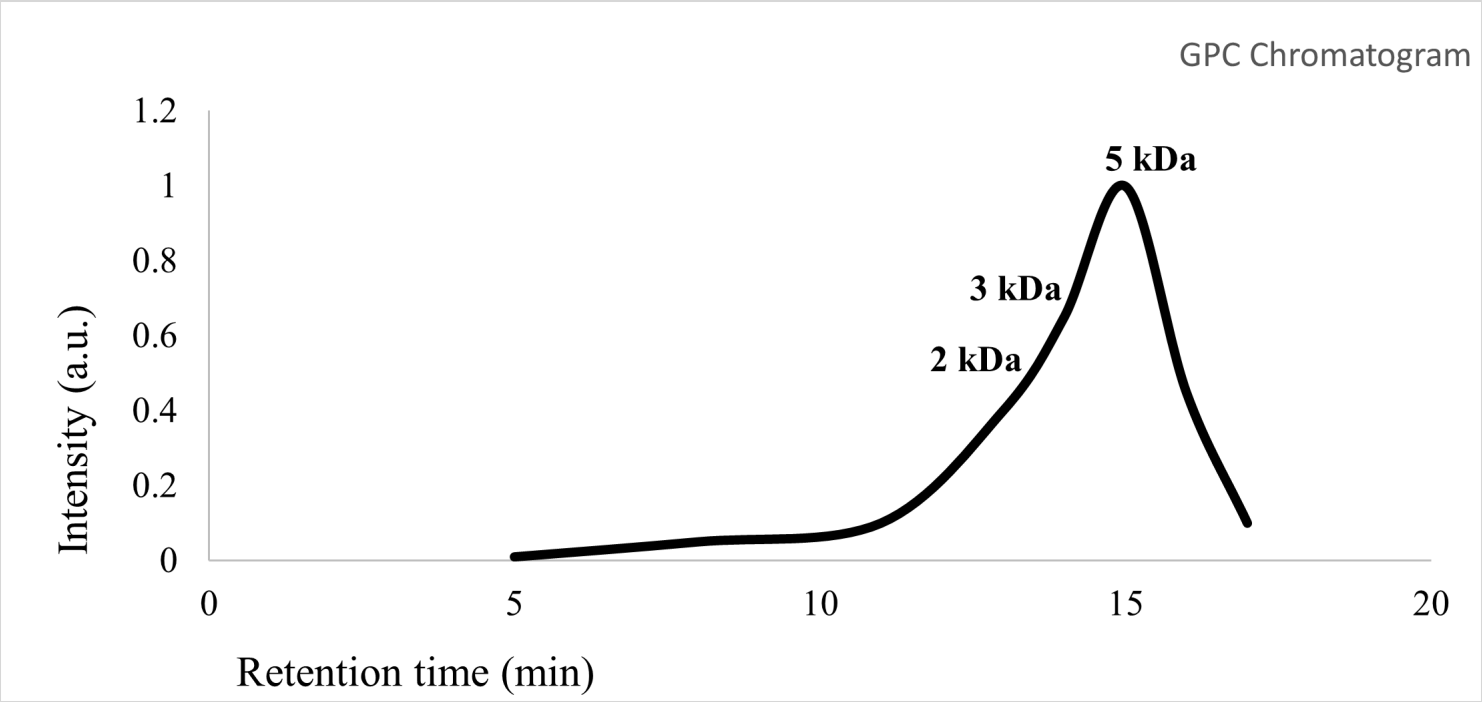


Figure 4

GPC chromatogram of the synthesized acrylate-urethane hybrid copolymer. The monomodal elution profile indicates high macromolecular homogeneity with a primary distribution exceeding 5 kDa.

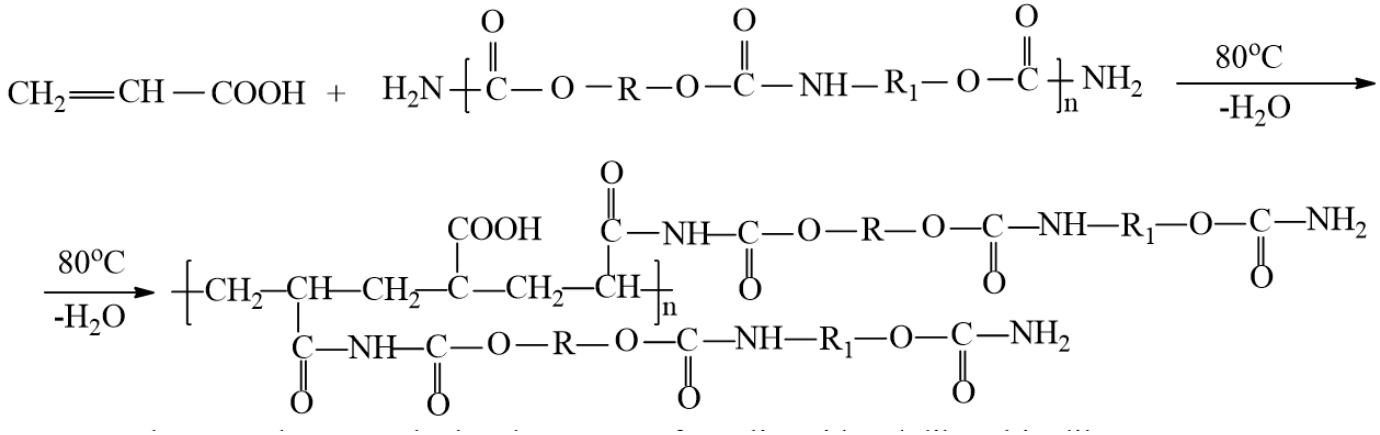


Figure 5

Unnumbered image in the 2. Experimental section section.