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Free Radical Copolymerization of Acrylic Acid And 2-Ethoxyethyl Methacrylate: Synthesis, Mechanism, Characterization, Reactivity Ratios, Microstructure and Potential Applications

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Abstract

This study reports the free radical copolymerization of acrylic acid (AA) and 2-ethoxyethyl methacrylate (2-EOEMA) using benzoyl peroxide as the initiator in acetone under a nitrogen atmosphere. The copolymers were synthesized at low conversion (~15%) to facilitate accurate determination of monomer reactivity ratios. The copolymerization mechanism was investigated and confirmed through FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy, revealing the successful incorporation of both monomers. Solubility studies demonstrated that increasing the AA content enhances water solubility, making the copolymers suitable for surface-active and biomedical applications.

Reactivity ratios were calculated using the Fineman-Ross (F-R) and Kelen-Tüdös (K-T) methods based on FT-IR spectral data, yielding average values of r_1 (AA) = 0.7391 and r_2 (2-EOEMA) = 0.2242, indicating a random copolymerization tendency ($r_1 \cdot r_2$ = 0.1652). Azeotropic composition analysis and sequence distribution calculations further supported the random nature of the copolymer, with 2-EOEMA showing higher reactivity. The copolymer microstructure was also analyzed by evaluating mean sequence lengths and monomer distribution along the polymer chain.

These findings suggest that AA/2-EOEMA copolymers, due to their tunable solubility and monomer composition, hold promise for applications in drug delivery, coatings, and as surface-active agents.

Keywords: Free Radical Copolymerization, Acrylic Acid, 2-Ethoxyethyl Methacrylate, Spectroscopic Characterization, Reactivity ratios, Water Solubility and Biomedical Applications.

1. Introduction

The copolymerization of two or more monomers is an excellent method for the preparation of macromolecules with specific chemical structures and for the control of properties such as monomer ratio, solubility, polarity, and hydrophilic/hydrophobic balance. For statistical copolymers, the monomer sequence distribution and compositional heterogeneity in and among the copolymer chains have a profound influence on the behavior and physical properties of the materials [1-6]. The poly(DMA-co-AAc) copolymer has a high swelling ability in an aqueous solution, the acrylic acid (AA; CH2=CHCOOH) monomer has been widely investigated for its applications in various fields [7-10]. The AA based polymers have good biocompatibility, low toxicity, good film forming and adhesive

characteristics [11]. It is also used as a comonomer in surface-active copolymerizations mainly because of its good amphilic character [12, 13]. Acrylic acid contains a highly polar carboxylic acid group, which confirms the hydrophilic nature [14]. Acrylic Acid and several acrylate based monomers [Methyl Aacrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and Methyl Methacrylate (MMA)] are used for the synthesis of functionalized copolymers with well-defined properties [15-17], which are potentially useful materials with specific technological, biomedical applications such as in the preparation of membranes for ultrafiltration /drug delivery, anticoagulant films and surface-active agents [18]. Another alkene monomer, 2-Ethoxyethyl Methacrylate (2-EOEMA; $H_2C=C(CH_3)CO_2CH_2CH_2OC_2H_5$) is a dual functional group monomer, which has both ether and ester groups as compared to most of the vinyl acrylic monomers. These groups not only impart flexibility into the polymer, but also improve its processability and handling [19], and improve compatibility in blends due to hydrogen bonding [20]. Because of their soft and flexible nature, 2-EOEMA based copolymers and terpolymers could be better candidates as surfactants, and, hence, are extensively studied in biomedical applications, controlled drug release studies, contact lenses and other products with good gas transfer properties applications [21-23].
The MMA-AA copolymers were obtained by a free radical polymerization method described by A.A. Barba *et al.* [24]. The use of MMA as a comonomer is an alternative way of inserting AA into the fiber structure. The copolymer of MMA-AA has potential applications in bone implants, surgical and also in the textile products [25]. The poly (styrene-methyl methacrylate-acrylic acid) was used for making super capacitors [26]. The free radical copolymerization MMA-2EOEMA were carried out using 2,2-azo – bisiso butyro nitrile as initiator and the reactivity ratios are evaluated[27]. The chemical structure of a copolymer depends on the two-monomer units, which are distributed along macromolecular chains. This distribution is a direct consequence of each monomer's reactivity in the polymer molecules [28]. Determination of the monomer reactivity ratios with small confidence intervals requires sensitive analytical techniques, careful planning of experiments, and the use of statistically valid methods of estimation [29, 30]. In order to calculate the rate of polymerization or polymer productivity and copolymer composition, monomer reactivity ratios must be known [29]. Reactivity ratios were determined by F-R [31] and K-T [32] methods using the data obtained by IR analysis. The reported investigation describes the synthesis of AA-EOEMA copolymers by freeradical polymerization and the characterization of their structures by FT-IR, 1H-NMR and 13C-NMR spectroscopic techniques. Reactivity ratios calculated are also presented here.

2. Materials and Methods

2.1 Materials

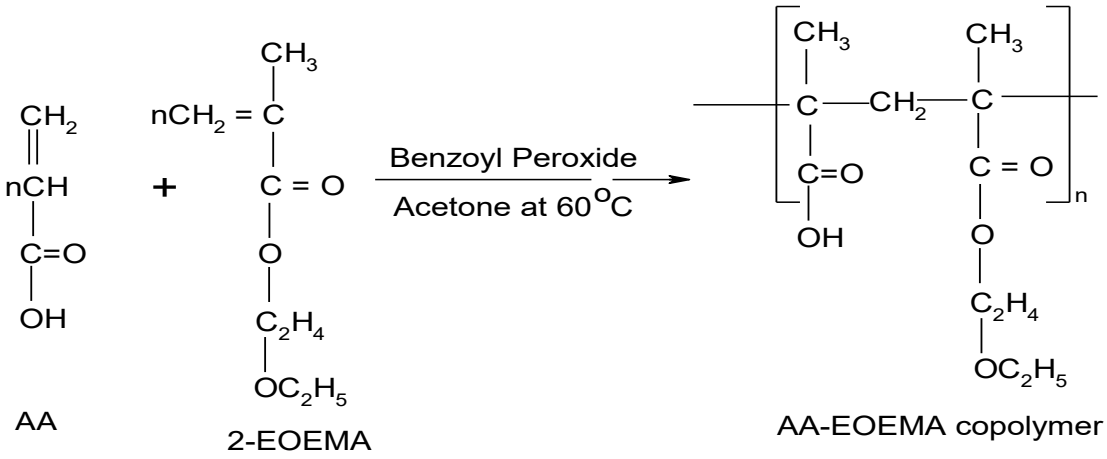
Acrylic acid (AA) and 2-ethoxyethyl methacrylate (2-EOEMA) were procured from Sigma-Aldrich Chemical Co., USA. Inhibitors present in both monomers were removed using Fuller's earth. Benzoyl peroxide (BPO), obtained from S.D. Fine Chemicals, was recrystallized from a chloroform–methanol mixture and dried under high vacuum at room temperature for 24 hours. Organic solvents including methanol, chloroform, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, 1,4-dioxane, cyclohexane, carbon tetrachloride, ethyl acetate, isobutyl acetate, diethyl ether, *n*-hexane, and benzene (all ≥99.9% purity) were used as received from E. Merck Chemicals, Mumbai, India.

2.2 Synthesis of AA/2-EOEMA Copolymer

The copolymerization of acrylic acid (AA, M_1) and 2-ethoxyethyl methacrylate (2-EOEMA, M_2) was conducted in acetone under a nitrogen atmosphere. A 1:1 molar ratio of AA and 2-EOEMA was used.

The reaction mixture consisted of the monomers (AA and 2-EOEMA), acetone (70% by volume), and benzoyl peroxide (0.5 wt%) as the free-radical initiator. The total volume was placed in a 100 mL three-necked round-bottom flask equipped with a reflux condenser, nitrogen inlet, and magnetic stirrer.

The flask was immersed in an oil bath maintained at 60 °C, and the reaction was carried out under a nitrogen atmosphere to prevent inhibition by oxygen. The copolymerization was allowed to proceed until high monomer conversion (approximately 15% ± 0.2%**)** was reached, which typically required 7–8 hours. Upon completion, the reaction mixture was cooled to room temperature to terminate the polymerization. The resulting yellow, viscous copolymer product was precipitated in excess diethyl ether to remove unreacted monomers and impurities. The precipitated copolymer was then collected by filtration and dried under vacuum at 40 °C until a constant weight was obtained.



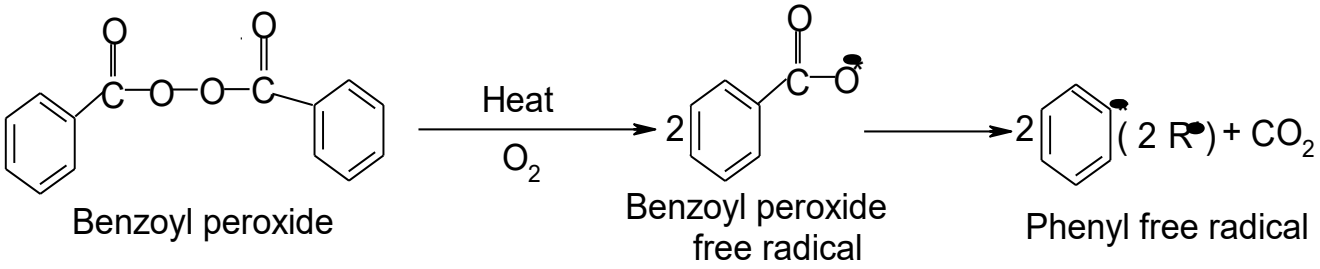
Scheme-1: General reaction for the synthesis of AA/2-EOEMA copolymer

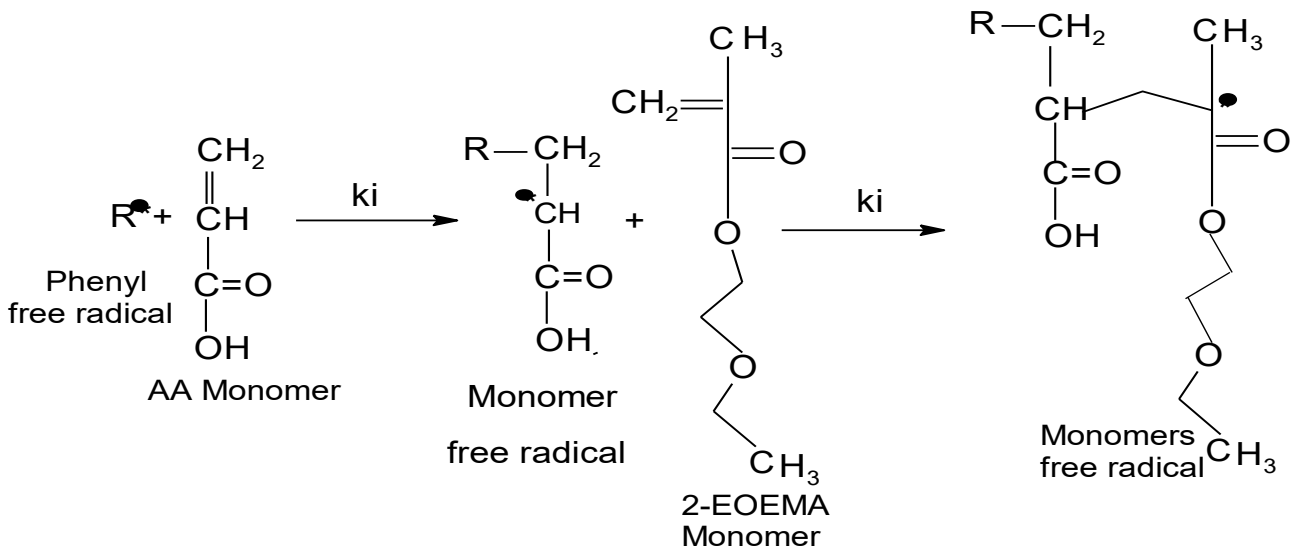
2.3 Free Radical Mechanism of AA/2-EOEMA Copolymer

The free radical mechanism of AA/2-EOEMA copolymer involving four steps

I. Initiation

This step involves the generation of free radicals (usually via a thermal initiator like AIBN or benzoyl peroxide).

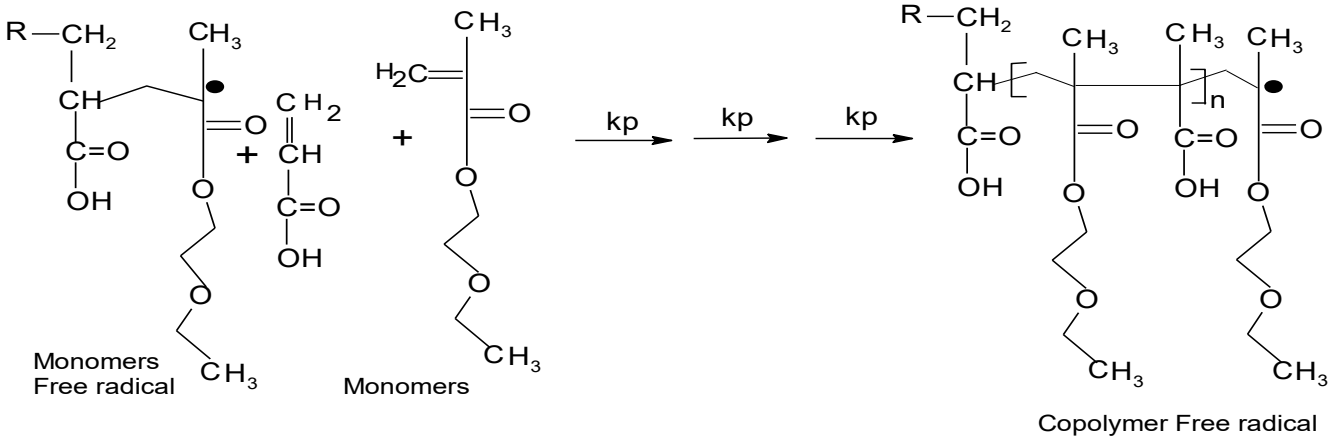




Scheme-2: Initiation reaction of AA/2-EOEMA copolymer
Where: R * = Phenyl free radical and ki = The rate of initiation

II. Propagation

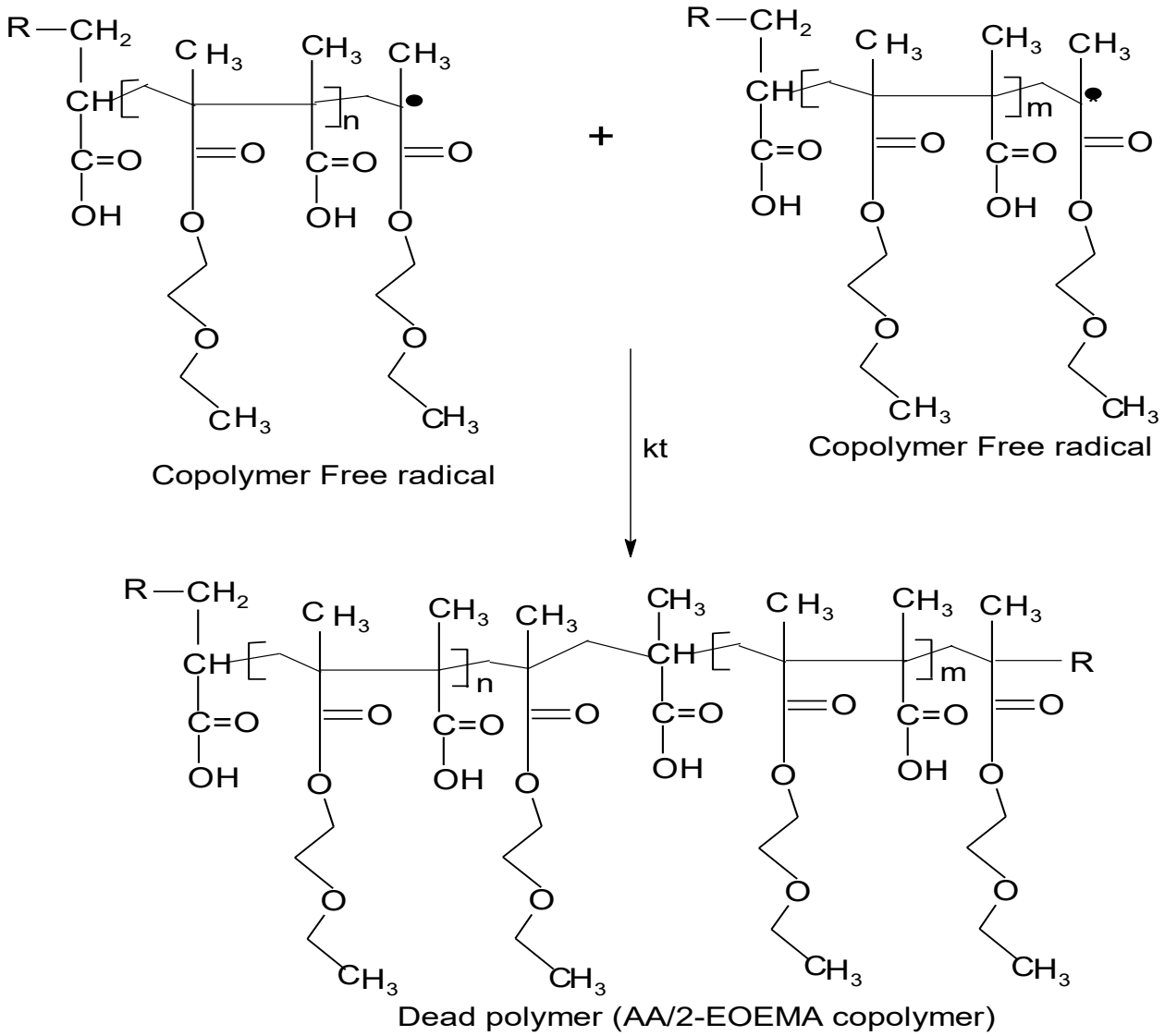
The growing radical adds to more monomer units, alternating or randomly incorporating AA and 2-EOEMA depending on feed ratio and reactivity.



Scheme-2: Propagation reaction of AA/2-EOEMA copolymer
Where: kp= The rate of propagation

III. Termination by combination:

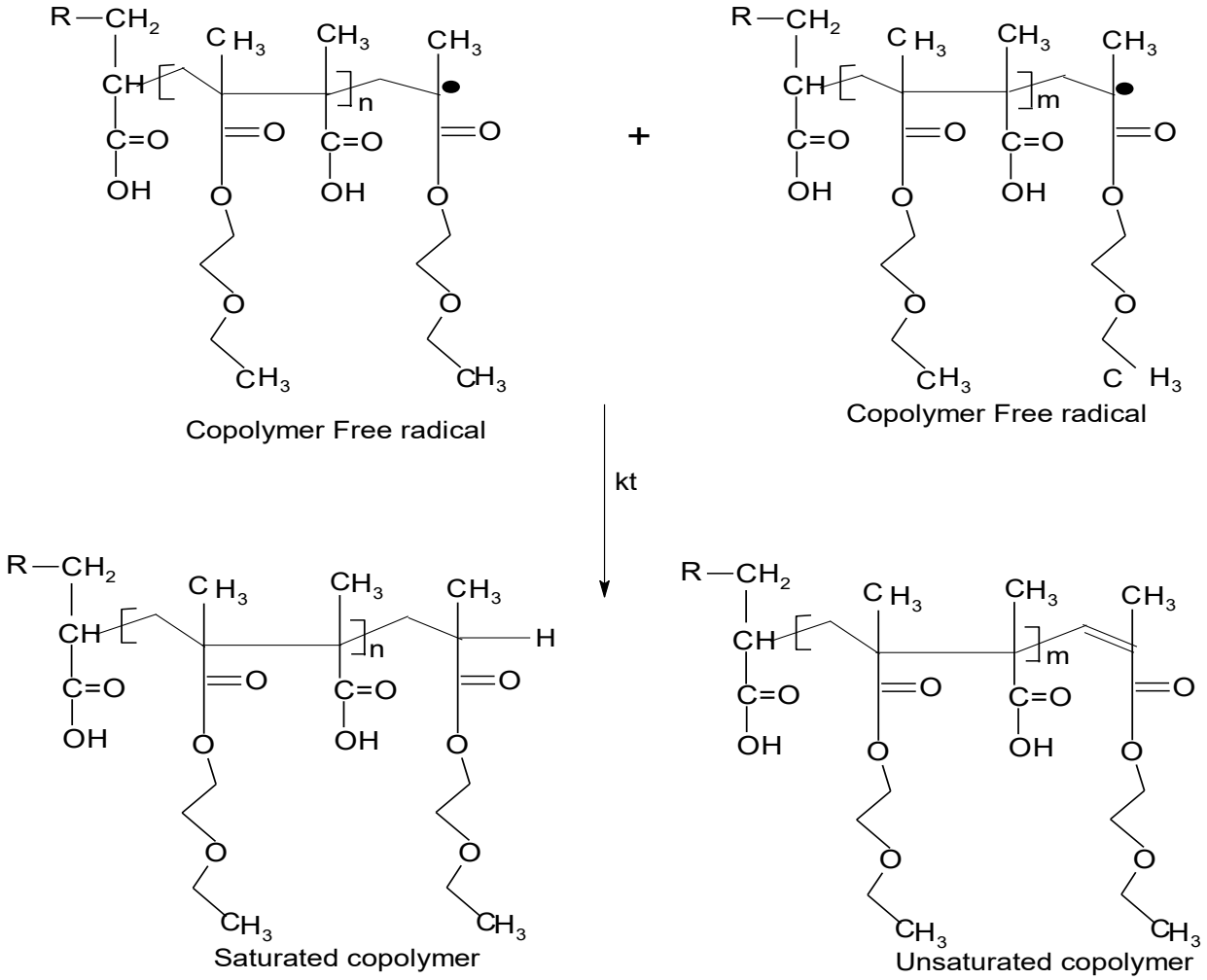
At low temperatures, termination by combination dominates in AA/2-EOEMA copolymerization due to reduced radical mobility and suppressed disproportionation.



Scheme-3: Termination by combination reaction of AA/2-EOEMA copolymer
Where kt = The rate of termination

IV. Termination by Disproportionation (more prevalent at higher temperatures)

AA/2-EOEMA copolymerization involves one polymer radical abstracting a β-hydrogen from another, forming one saturated and one unsaturated chain end, typically favored due to the bulky methacrylate (EOEMA) structure.



Scheme-4: Termination by Disproportionation reaction of AA/2-EOEMA copolymer

2.4 Solubility Studies

The copolymers demonstrate complete solubility in most polar solvents, while remaining insoluble in non-polar solvents. A key observation is that increasing the content of 2-ethoxyethyl methacrylate (2-EOEMA) in the copolymer leads to a reduction in its water solubility. Acrylic acid (AA) is inherently highly soluble in water. However, copolymers synthesized with varying AA:2-EOEMA molar ratios exhibit distinct solubility behaviors: Ratios of 1:1, 2:1, 3:1, and 4:1 (AA:2-EOEMA): These copolymers are completely insoluble in water**,** Ratios of 5:1 and 6:1: These copolymers are partially soluble in water**,** Ratios above 6:1: Copolymers with higher AA content become fully water-soluble**.** This variation in water solubility, governed by the acrylic acid content, suggests potential applications for these copolymers as surface-active agents or in other formulations requiring tunable solubility profiles.

3. Spectroscopy Analysis

3.1 Fourier Transform Infrared (FT-IR) Spectral Studies

The FT-IR spectrum of the AA/2-EOEMA copolymer is presented in Figure 4.2.1. The observed characteristic absorption bands indicate the presence of various functional groups from the copolymer components: Ester carbonyl (C=O) group from 2-EOEMA shows a strong absorption peak at 1712.18 cm^{-1}**,** Ether group (–CH_2–O–CH_2–) of 2-EOEMA is identified by the absorption peak at 1211.08 cm^{-1}**,**

Alkene (C=C) group, attributed to ethylene units (C_2H_4), appears at 771.82 cm^{-1}**,** Alkyl (–C–H) bending vibrations, contributed by both AA and 2-EOEMA, are observed at 1363.61 cm^{-1}**,** Alkane (C–C) skeletal vibrations are indicated by the peak at 661.31 cm^{-1}**,** Carboxylic acid (O–H and C–H stretching) from AA is observed in the broad absorption range between 2811.18 cm^{-1} and 3020.53 cm^{-1}**.** These spectral features confirm the successful incorporation of both acrylic acid (AA) and 2-ethoxyethyl methacrylate (2-EOEMA) units in the copolymer structure.

3.2 Proton Nuclear Magnetic Spectroscopy (H^1-NMR) Analysis of the AA-co-2-EOEMA Copolymer

The ^{1}H-NMR spectrum of the synthesized copolymer provides essential information about the proton environments in both the AA and 2-EOEMA units. The observed chemical shifts (δ, in ppm) correspond to the following structural features:

Main Chain Signals: Backbone methylene protons (from both AA and 2-EOEMA units): **δ** = 1.89–2.09 ppm These signals overlap due to similar environments and compositional / configurational sequences, making individual assignments difficult.

2-EOEMA Unit Assignments: Methyl groups**: δ** = 0.88–1.29 ppm Typical terminal methyl protons, possibly from ethyl side chains. Keto group ($COCH_3$)**: δ** = 2.79 ppm, deshielded due to the electron-withdrawing carbonyl group adjacent to the methylene, methylene groups (–CH_2–) near the ether oxygen**: δ** = 3.50–3.69 ppm Corresponds to protons in the –CH_2CH_2O– side chain of 2-EOEMA Ether group (–CH_2–O–CH_2–) **:δ** = 4.12 ppm indicates protons directly bonded to carbon adjacent to oxygen (strongly deshielded).

Side Chain and Functional Group Protons: Methylene (–CH_2–) adjacent to polar groups (AA and 2-EOEMA)**:** δ = 7.30–8.20 ppm likely affected by neighboring electronegative atoms or conjugated systems, carboxylic acid proton (–COOH) from AA units**:** δ = 10.3–10.85 ppm highly deshielded, typical of acidic protons; broad signal due to hydrogen bonding. Conjugated alkene protons (if present)**:** δ = 7.35–8.10 ppm may overlap with aromatic or vinylic proton signals, suggesting possible unsaturation or residual monomer.

3.3 C^{13} Nuclear Magnetic Resonance Spectroscopy (C^{13}-NMR)

The structure of the copolymer was confirmed by C^{13}-NMR spectroscopy, as shown in Figure 4.1.3**.** The major chemical shifts observed in the spectrum are assigned as follows: Carbonyl carbon (>C=O**)** of 2-EOEMA units appears at δ 167.48 ppm**, c**arboxylic acid carbon of the acrylic acid (AA) unit resonates at δ 172.12 ppm**,** Ether group (–CH_2–O–CH_2–) of 2-EOEMA is observed at δ 66.67 ppm**,** Methoxy group (–O–CH_3) of 2-EOEMA shows a signal at δ 64.04 ppm**,** Side-chain methylene carbons (–CH_2–) of both AA and 2-EOEMA units appear in the region δ 125.63–128.14 ppm, **o**lefinic carbons (=CH<) of both monomer units are found in the region δ 133.55–136.31 ppm, Ethylene glycol segment (–CH_2CH_2–O–) of 2-EOEMA appears at δ 68.39 ppm**, t**he region from δ 68.39–15.16 ppm is complex due to overlapping signals**,** likely arising from aliphatic carbon resonances in the polymer backbone and side chains**,** Ethyl group (–CH_2CH_3) of 2-EOEMA resonates at δ 15.16 ppm**,** Methyl groups (–CH_3) of 2-EOEMA appear at δ 18.31 ppm. These chemical shifts collectively confirm the successful incorporation of both AA and 2-EOEMA units in the copolymer chain.

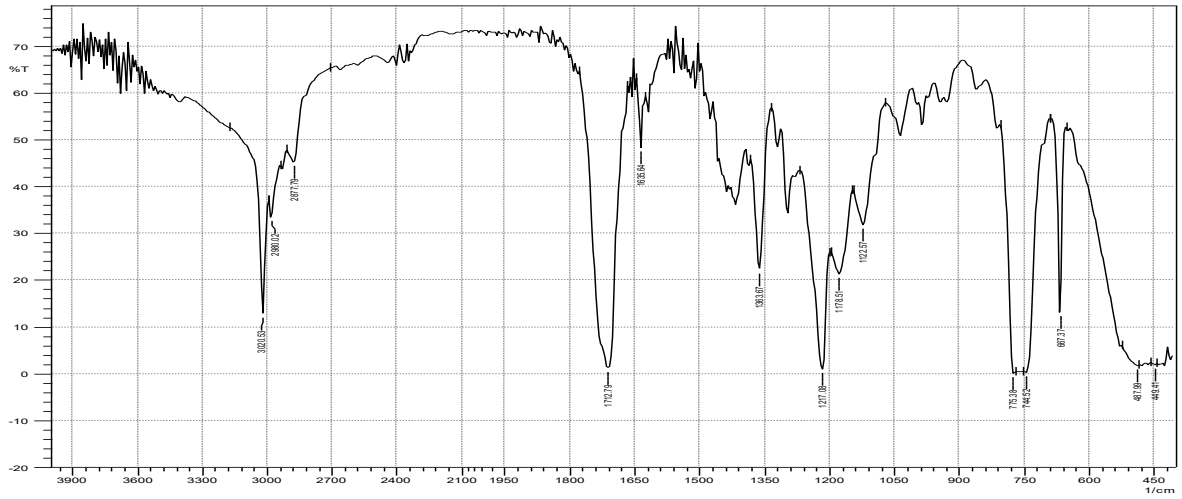


Figure: FT-IR Spectra of AA copolymer

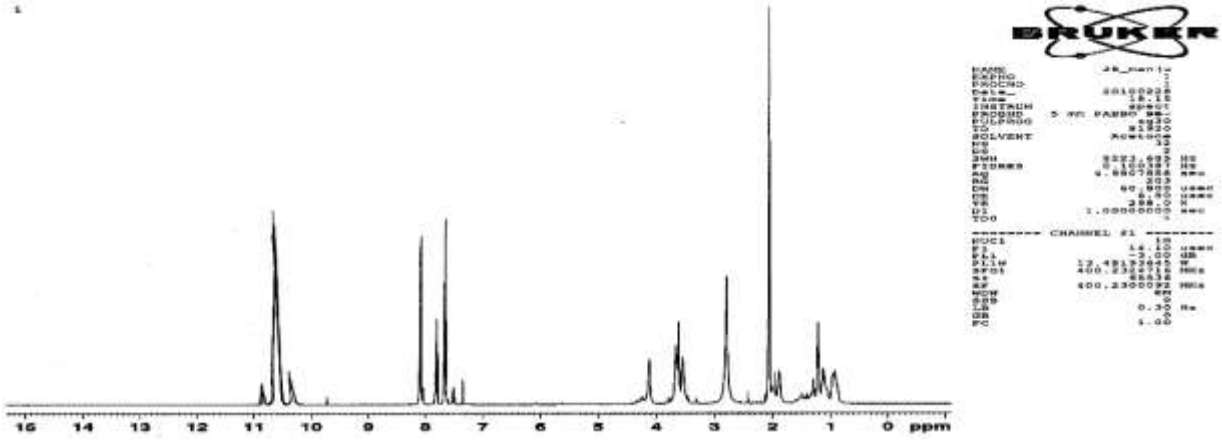


Figure: H^1-NMR Spectra of AA copolymer

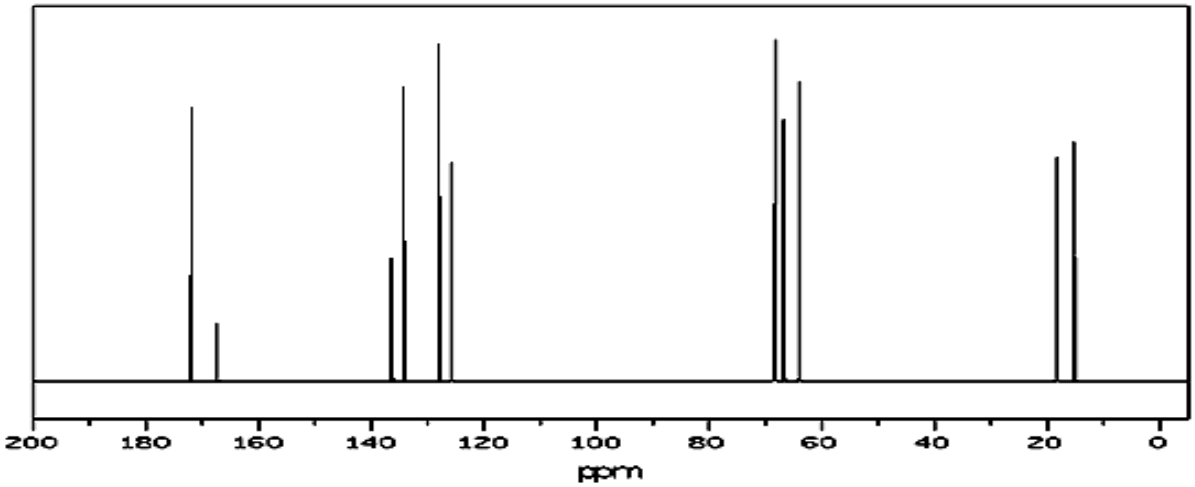


Figure: C^{13}-NMR-Spectra of AA copolymer

3.4 Yield and Purity of the Copolymers

The copolymerization of acrylic acid (AA, M1) and 2-ethoxyethyl methacrylate (2-EOEMA, M2) was carried out following the same procedure as that used for the MMA/2-EOEMA copolymer. The

composition of monomers and the corresponding yields and purities of the resulting copolymers are presented in Table

Table 1: Yield and Purity of the Copolymers

Sample	Monomer Composition		Solvent	Copolymer yield		Purity
	AA(M_1) (in gm)	2-EOEMA(M_2) (in gm)	1,4 dioxane (in gm)	Weight (in gm)	Percentage (in %)	Percentage (in %)
1	10.006	19.994	70	4.5	15.00	99
2	12.507	17.493	70	4.498	14.99	
3	15.009	14.991	70	4.495	14.98	
4	17.510	12.490	70	4.492	14.97	
5	20.012	9.988	70	4.488	14.96	
6	22.513	7.487	70	4.483	14.94	

The percentage conversion (yield) is calculated based on the total weight of monomers used, not including the solvent. This approach avoids underestimation of conversion rates, which would occur if the solvent mass were included. All samples show approximately 15% conversion, with high purity in the isolated copolymer.

3.5 Copolymer Composition Determination via FT-IR Spectroscopy

The monomer composition in the copolymer was determined using FT-IR spectroscopy by analyzing characteristic absorption bands of functional groups from each monomer. The carbonyl group of the copolymer appears at 1728 cm^{-1}, the ether group of 2-EOEMA shows a peak at 1196 cm^{-1}, and the carboxylic acid group of acrylic acid (AA) is observed at 3498 cm^{-1}. By measuring the absorbance of these peaks, the concentrations of AA and 2-EOEMA in the copolymer were quantified. The data showed that the ether peak intensity increased with higher 2-EOEMA content. Using these absorbance values, the copolymer composition was calculated using specific equations, enabling the determination of the relative amounts of AA and 2-EOEMA in the product. By calculating the absorbance at these wavelengths, the relative concentrations of AA and 2-EOEMA in the copolymer can be determined. The data were calculated according to the following equations.

The monomer composition of AA (acrylic acid) and 2-EOEMA in copolymers was determined using FT-IR spectroscopy by analyzing characteristic absorption peaks corresponding to each monomer. The carboxylic acid group of AA showed a peak at 3498 cm^{-1}, while the ether group of 2-EOEMA appeared at 1196 cm^{-1}. By measuring the absorbance of these peaks and normalizing with the respective molecular weights, the mole fractions of AA and 2-EOEMA in the copolymer were calculated using the provided equations.

$$m_1 = \frac{\frac{A^{3498}}{M_{AA}}}{A^{1196}/M_{EOEMA} + A^{3498}/M_{AA}} \times 100$$

$$m_2 = \frac{A^{1196}/M_{EOEMA}}{A^{1196}/M_{EOEMA} + A^{3498}/M_{AA}} \times 100$$

The method showed that with increasing 2-EOEMA content in the feed, the absorbance at 1196 cm^{-1} increased correspondingly, confirming the compositional changes in the copolymer. The copolymer

compositions obtained from FT-IR analysis were compared with feed compositions by plotting the mole fractions of each monomer, demonstrating the relationship between feed ratio and copolymer composition.

The composition of these copolymers was analyzed using FT-IR spectroscopy. The absorbance (A) was calculated as the logarithm of the inverse of transmittance (T), i.e., $A=\log_{10}(1/T)$.

The molecular weights of AA and 2-EOEMA monomer units are denoted as M_{AA} and $M2_{-EOEMA}$ respectively. The mole fractions of AA (M1) and 2-EOEMA (M2) in the feed were compared with the mole fractions in the resulting copolymer (m1 and m2) based on FT-IR data.

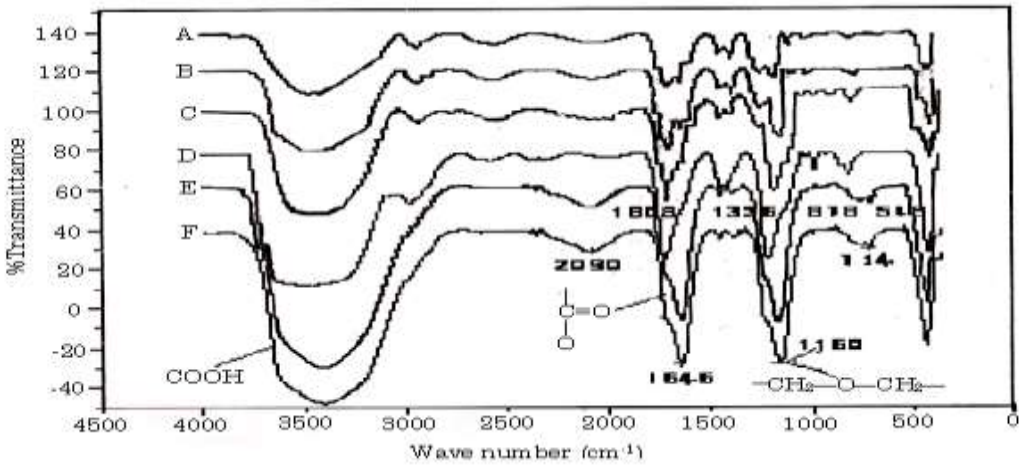


Figure: FT-IR spectra were recorded for copolymers prepared with different feed ratios of AA to EOEMA: 50:50, 66.7:33.3, 75:25, 80:20, 83.3:16.7, and 85.7:14.3. These spectra help determine how the monomer feed composition affects the copolymer composition.

3.6 Determination of Monomer Reactivity Ratios

Copolymerization reactivity ratios of AA and 2-EOEMA in the products were determined using the standard Fineman-Rose (F-R) and Kelen-Tudos (K-T) methods based on FT-IR spectral data respectively.

Table 2: F-R and K-T parameter for copolymer by FTIR data

Sample no	$x=M_1/M_2$	$y=m_1/m_2$	$G=x(y-1)/y$	$F=x^2/y$	$\eta=G/(\alpha+F)$	$\xi=F/(\alpha+F)$
A	1.0000	0.3102	-2.2237	3.2240	-0.2000	0.2900
B	2.0030	0.6213	-1.2209	4.3117	-0.1500	0.3533
C	3.0000	0.9305	0.2241	9.6722	0.0117	0.5507
D	4.0000	1.2407	0.7760	12.896	0.0648	0.6204
E	4.9880	1.6630	1.9886	14.9612	0.0959	0.6547
F	5.9932	1.8590	2.7692	19.3201	0.1400	0.7091

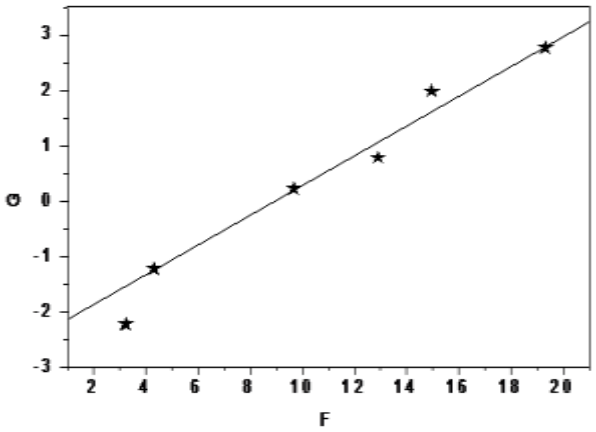


Fig. F-R plot of G vs. F

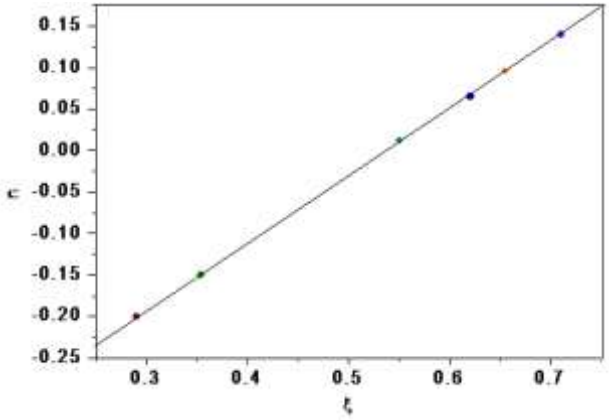


Fig K-T plot of. η vs. ξ

The F-R method uses the relationship between parameters G and F, while the K-T method analyzes parameters η and ξ for improved linearity.

3.7 Copolymer Microstructure

The copolymer microstructure and sequence length distribution of monomers in the formation of the copolymer. Here, we have attempted to calculate the sequence length distribution of the resulting copolymer. The probability of finding the sequence of $N_{EOEMA\ (n)}$ and $N_{AA\ (n)}$ units is calculated as following equations·

$N_{AA\ (n)} = P_{11}^{n-1}(1–p_{11})$

$N_{EOEMA\ (n)} = P_{22}^{n-1}(1–p_{11})$

where P_{11} and P_{22} are the probability of an AA (or 2-EOEMA) unit, these probabilities (Table-4.2.4) are calculated with the following equations.

$$P_{11} = \frac{r_1}{R + r_1}$$

$$P_{22} = \frac{r_2}{R + R_2}$$

where R is the mole ratio of AA to 2-EOEMA in the feed, the values of $N_{AA\ (n)}$ and $N_{EOEMA\ (n)}$ were calculated for the obtained copolymer at an equimolar feed. In our case, we observed that the copolymer contains predominantly a sequence of 2-EOEMA, which is in agreement with higher reactivity of 2-EOEMA.

The mean sequence lengths μ_{AA} and $\mu_{2\text{-EOEMA}}$ were also calculated using the following relation.

$\mu_{AA} = 1 + r_1 (M_1/M_2)$

$\mu_{2\text{-EOEMA}} = 1 + r_2 (M_2/M_1)$

The value of μ_{AA} and $\mu_{2\text{-EOEMA}}$ are presented in Table 4.2.4. The $\mu_{2\text{-EOEMA}}$ values increases from 1.7826 to 5.6902 in the copolymer with an increase of 2-EOEMA concentration in the feed. Higher 2-EOEMA content found in the synthesized copolymer and correlated with the calculated r_1 and r_2 values indicates that the AA/2-EOEMA copolymer composition is enriched with the 2-EOEMA monomer

Table 3: Statistical data for copolymer

Sample	P11	P22	μ 2-EOEMA	μ AA
A	1.7826	0.4542	1.7826	1.2272
B	4.7946	0.3403	2.5676	1.1133
C	9.7826	0.3026	3.3478	1.0756
D	16.7831	0.2837	4.1304	1.0567
E	25.6632	0.2725	4.9036	1.0455
F	36.6990	0.2649	5.6902	1.0379

The statistical analysis of the AA/2-EOEMA copolymer microstructure reveals a strongly segmental and EOEMA-rich architecture driven by significant differences in monomer reactivity. 2-EOEMA exhibits a pronounced tendency to self-propagate, forming extended sequences within the copolymer, while AA is incorporated more sporadically, resulting in shorter and less frequent sequences. As the 2-EOEMA content in the feed increases, the copolymer composition shifts accordingly, further enriching the EOEMA segment content. These findings confirm that the copolymerization process does not yield a random distribution of monomers but rather a microstructure with distinct block-like EOEMA-rich regions, governed primarily by monomer reactivity and feed composition.

3.8 Potential Applications

These materials offer versatile, stimuli-responsive properties ideal for biomedical and smart material applications. Their tunable solubility, adhesion, and rheology enable precise control in various formulations. Biocompatibility and flexibility enhance their suitability for drug delivery and tissue engineering. Overall, they provide a multifunctional platform for advanced, responsive systems. The various potential applications of copolymers are summarized in the table below.

Property	Description	Potential Applications
Swellable, flexible, pH-responsive, biocompatible	Responsive to pH changes, flexible structure, safe for biomedical use	Targeted and oral drug release
Stimuli-responsive materials	Reacts to environmental stimuli such as temperature, pH, etc.	Biomedical applications, tissue engineering
Amphiphilic tunable HLB structure	Balances hydrophilic-lipophilic properties, can be adjusted	Emulsifiers, dispersants, stabilizers
Tunable solubility and adhesion	Adjustable solubility and adhesion properties	Responsive films, protective layers
AA-based adhesion	Adhesion based on acrylic acid components	Adhesive applications, biomedical interfaces
EOEMA flexibility	Flexibility from ethoxyethyl methacrylate units	Flexible films, coatings
Functionalizable, responsive	Can be chemically modified for specific functions and responds to	Smart materials, sensors, controlled release systems

	stimuli	
Rheology control	Ability to modify flow and deformation behavior	Injectable gels, coatings, and formulation tuning
Compatibility	Compatible with other materials and formulations	Composite materials, multi-component systems

4. Conclusions

AA/2-EOEMA copolymers were successfully synthesized via free radical solution polymerization using benzoyl peroxide as an initiator. Spectroscopic analyses (^1H-NMR, ^13C-NMR, and FT-IR) confirmed the formation and structure of the desired copolymers. The reactivity ratio analysis revealed a significant preference for 2-EOEMA incorporation over AA, resulting in a segmental copolymer microstructure characterized by EOEMA-rich domains interspersed with shorter AA sequences. This non-random distribution imparts the copolymers with tunable solubility and physicochemical properties, which are highly dependent on the monomer feed composition. In particular, increasing the 2-EOEMA content enhances polymer solubility in polar solvents and modifies the hydrophilic–hydrophobic balance, making these materials promising for applications where tailored solubility and segmental structure are beneficial. The tunable water solubility, coupled with the ability to control microstructural architecture through monomer feed and reactivity, makes these AA/2-EOEMA copolymers strong candidates for functional applications such as surface-active agents and targeted drug delivery systems, especially in oral formulations. These findings underscore the value of understanding and leveraging monomer reactivity differences to design polymers with specific, application-driven properties.

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