

auf die Gestalt der Verteilung hat. Damit ist k kein echter Parameter der logarithmischen Verteilung, sondern bestimmt lediglich die mathematische bzw. physikalische Bedeutung des Lageparameters α_k und dient zur Unterscheidung der Spezialfälle. Eine logarithmische Verteilung ist durch eine beliebige Anzahl von k - und α_k -Werten mit einem dazugehörigen σ darstellbar. Eine Änderung von k bewirkt nur eine Verschiebung der Verteilungskurve unter Beachtung der Normierung, so daß ausschließlich der Breitenparameter σ die Gestalt der Kurve bestimmt. Aus diesen Tatsachen ergab sich die wesentliche Schlußfolgerung, daß die Wahl eines speziellen k -Wertes die Allgemeingültigkeit der erhaltenen Resultate nicht beeinflußt. Damit ist die Möglichkeit der Anpassung der logarithmischen Verteilung an die jeweils verwendete Meßmethode durch Einführung eines geeigneten k -Wertes gegeben. Am Beispiel der Lichtstreuung wird demonstriert, wie eine solche Anpassung realisiert werden kann.

Die beiden bekanntesten Spezialfälle der logarithmischen Verteilung sind für $k = 0$ die ZOLD (zeroth-order logarithmic distribution) und für $k = -1$ die logarithmische Normalverteilung. Schließlich wurde die logarithmische Verteilung für die Beschreibung von Teilchengrößenverteilungen von Kugelsystemen verwendet und die Beziehung zur Verteilung von Teilchenmassen erläutert.

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Kurze Mitteilungen

Copolymerization of acryloyl chloride with 2-hydroxypropyl methacrylate

1. Introduction

Copolymers of acryloyl chloride with methyl methacrylate, styrene, acrylonitrile, chloroethylene have been prepared by other authors [1–4] and the monomer reactivity ratios were calculated. We now report the results for copolymerization of acryloyl chloride (AC) with 2-hydroxypropyl methacrylate (2-HPMA).

The obtained copolymers are important for subsequent reactions, such as: with enzymes, antibiotics and other biological active substances.

2. Experimental

2.1. Monomers

Acryloyl chloride (AC) was prepared by reaction of acrylic acid and benzoyl chloride by the method of STEMPER et al. [5] (b.p. 72 to 74°C, at 740 mm Hg).

2-Hydroxypropyl methacrylate (2-HPMA) (Merck Schuchardt) was washed with 5% by wt. aqueous sodium hydroxide, dried and distilled at reduced pressure under nitrogen before use.

2.2. Solvents and catalyst

Dioxane was purified by refluxation on sodium, followed by distillation under nitrogen and finally kept on potassium hydroxide pellets. Petroleum ether was dried with calcium chloride and then distilled. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol several times (m.p. 103°C).

2.3. Copolymerization

Copolymerizations were carried out in dioxane solutions under nitrogen at 60°C, in joint-cup bottles. In all cases the total monomer concentration was of 15% by wt. and initiator (AIBN) of 1% by wt. toward monomers. After a given time the contents of bottles were poured into a large amount of petroleum ether to precipitate the copolymer. The resulting polymer was purified by repeated reprecipitation, using dioxane. Copolymer composition was determined by elemental analysis [6].

2.4. Measurements

The IR spectrum was recorded with Perkin-Elmer 577 infrared spectrophotometer (KBr pellets).

3. Results and discussion

Copolymerization results are presented in Table 1. All copolymerizations proceeded homogeneously. The copolymers were soluble in dioxane and insoluble in benzene, ether, chloroform, n-hexane. As can be seen in Table 1 the conversion increases

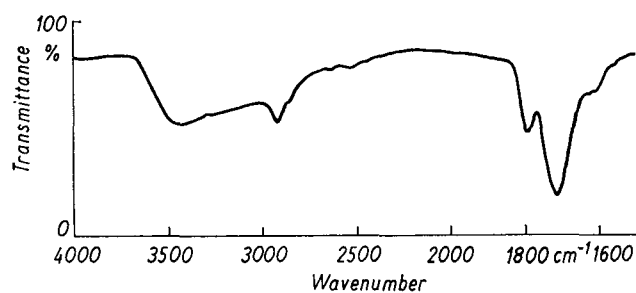


Fig. 1. IR spectrum of AC-2-HPMA copolymer

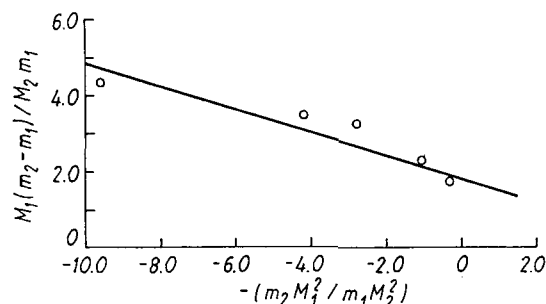


Fig. 2. Evaluation of r_{AC} and r_{2-HPMA} by FINEMAN-ROSS method

Table 1. Radical copolymerization of AC (M_1) with 2-HPMA (M_2) in dioxane

Exp.	AC in monomer feed (M_1) mole-fraction	Time h	Conversion %	Cl-content %	AC in copolymer (m_1) mole-fraction
1	0.150	3	11.00	1.62	0.08250
2	0.285	3	14.20	2.58	0.12906
3	0.405	3	16.50	2.92	0.14524
4	0.515	3	15.42	3.95	0.19276
5	0.614	3	19.82	4.33	0.20993
6	0.614	5	46.22	4.47	0.21616
7	0.614	8	81.04	4.49	0.21750

while AC molar fraction does not modify with increasing reaction time.

A typical IR spectrum of copolymers is shown in Figure 1. The characteristic frequencies for carbonyl groups in acid chlorides, hydroxyl groups and carbonyl groups in esters can be observed.

Monomer reactivity ratios, r_{AC} and r_{2-HPMA} , were determined by both FINEMAN-ROSS [7] and KELEN-TÜDÖS [8]

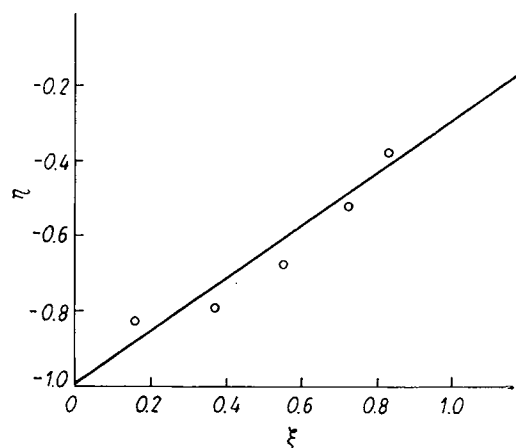


Fig. 3. KELEN-TÜDÖS plot for copolymerization of AC and 2-HPMA

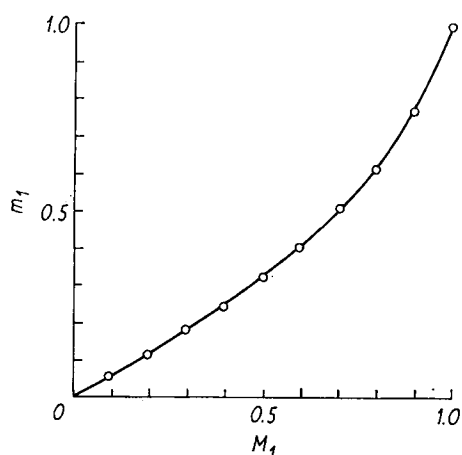


Fig. 4. Copolymerization of AC and 2-HPMA; composition curve built up according to the r -values obtained by FINEMAN-ROSS method

Table 2. Copolymerization reactivity ratios of AC (r_{AC}) and 2-HPMA (r_{2-HPMA}) calculated by Fineman-Ross (F-R) and Kelen-Tüdös (K-T) methods

F-R		K-T		$r_{AC} \cdot r_{2-HPMA}$	
r_{AC}	r_{2-HPMA}	r_{AC}	r_{2-HPMA}	F-R	K-T
0.32	1.80	0.29	1.79	0.576	0.519

methods (Figures 2 and 3). The values which were obtained are presented in Table 2. The r_{AC} values are < 1 and those for r_{2-HPMA} are > 1 . This result shows that 2-HPMA growing species react preferentially with 2-HPMA molecules. AC growing ends exhibit a tendency to add 2-HPMA molecules.

In Figure 4 the theoretical curve calculated from the monomer reactivity ratios and the observed plots is shown. The copolymer is richer in 2-HPMA than the feed mixture, copolymerization leading to the gradual enrichment of monomer feed with AC.

4. Summary

Radical copolymerization of acryloyl chloride (AC) with 2-hydroxypropyl methacrylate (2-HPMA) in solution, at 60°C, using as initiator 2,2'-azoisobutyronitrile (AIBN) was investigated. The monomer reactivity ratios were calculated using FINEMAN-ROSS and KELEN-TÜDÖS methods. The effect of the time reaction on the conversion was also determined.

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