

Copolymerization of Alkyl Methacrylates with Triallyl Cyanurate. Determination of Monomer Reactivity Ratios

ANNA RYTTEL

Faculty of Chemistry, Technical University of Rzeszów, 35-959 Rzeszów, Poland

SYNOPSIS

The free-radical copolymerization of propyl, pentyl, hexyl, heptyl, octyl, and dodecyl methacrylates with triallyl cyanurate was investigated. The reactivity ratios were determined using the methods of Fineman–Ross and Kelen–Tüdös. The Alfrey–Price Q and e values for the methacrylates were also evaluated. The effect of the length of alkyl group in methacrylates on reactivity ratios is discussed.

INTRODUCTION

In a series of papers,^{1–6} we have described synthesis and some properties of copolymers of various acrylates and methacrylates with nitrogen-containing monomers, such as triallyl cyanurate,^{1–3} *N*-phenyl, *N*-tolylmaleimide,^{4,5} or *N*-vinylcarbazole.⁶ The aim of investigations was to improve some properties of acrylate and methacrylate polymers, mainly their thermal stability.^{7–9}

Here, we present further results of the investigations. The process of free-radical copolymerization of several methacrylates of straight-chain alkyl alcohols, propyl through dodecyl, with triallyl cyanurate are described. Reactivity ratios of the comonomers are calculated by using both the methods of Fineman–Ross¹⁰ and Kelen–Tüdös.^{11–13} The reactivity ratios are used to evaluate Q and e values for methacrylates according to the Alfrey–Price scheme.¹⁴ The effect of the length of alkyl chain in methacrylates on the reactivity ratios is discussed.

EXPERIMENTAL

Monomers

Propyl (PrMA), pentyl (PtMA), hexyl (HxMA), heptyl (HpMA), octyl (OcMA), and dodecyl (DdMA) methacrylates were synthesized by transesterification from methyl methacrylate and appro-

priate alcohols in the presence of *p*-toluenesulfonic acid as catalyst (concentrated sulfuric acid was used in the case of PrMA). Hydroquinone (0.3 mol) and copper flakes served as inhibitors.^{15,16} The reaction was carried out in a flask under 48-in. fractionated column filled with Rashig's rings and fitted with a condenser arranged to control reflux. The solvent was benzene and the temperature in the flask ranged from 94 to 110°C depending on alcohol used. After reaction, the cold mixture was neutralized, washed, dried, and then the solvents were distilled off in a rotary evaporator at about 20 mmHg. The ester was purified by fractional distillation under reduced pressure. For all methacrylates the yield was about 60%. The purity of monomers was checked by measuring their physical properties (see Table I) and by IR and NMR analyses.¹⁷

The synthesis of triallyl cyanurate (TAC) was described elsewhere.⁹ The nitrogen content determined by Kjeldahl's method was 16.8% (calculated 16.86%), mp 27–28°C, bp 137–140°C, $n_D^{20} = 1.5060$, $n_D^{25} = 1.5049$.

Benzoyl peroxide (BP), pure grade (Argon, Łódź, Poland), contained 86.5% of BP as analyzed according to Ref. 18.

Copolymerization and Copolymer Analysis

The copolymerization was carried out in bulk as follows. The appropriate amounts of comonomers were weighed and poured after dissolving initiator (BP) into 15 ± 2-mL glass ampules. The time of copolymerization was established experimentally. It was

Table I Physical Properties of Alkyl Methacrylates

Monomer	Bp (°C)/ mm Hg	d_4^{20} g/cm	n_D^{20}	Molecular Weight		Saponification Number	
				Calcd.	Found ^a	Calcd.	Found
PrMA	40/8	0.9060	1.4191	128.2	128.6	438	444
PtMA	77/17	0.8913	1.4277	156.0	154.0	359	362
HxMA	111/24	0.8833	1.4300	170.0	171.6	329	333
HpMA	62/4	0.8825	1.4322	184.3	182.9	304	305
OcMA	120/16	0.8830	1.4378	198.3	196.1	283	282
DdMA	179/14	0.8753	1.4450	254.4	222.2	221	219

^a From cryoscopic analysis in dioxane.

short enough to obtain conversion of monomers below 10% (0.6–6.6 h). After that time the ampules were removed from the bath, cooled down to room temperature, and broken into acetone. Copolymer was isolated and purified by two precipitation-dissolving cycles in acetone and methanol. It was then filtered, dried in vacuo at room temperature to constant weight and analyzed for nitrogen contents.

The content was determined by Kjeldahl's method.¹⁹ Each copolymer was analyzed three times. The results obtained in this way were reproducible within 0.3%. For pure TAC, the result of nitrogen analysis agreed with the calculated one. Two series of measurements for nine compositions were made for each pair of comonomers. The average results from the two series are presented in Tables II to VII.

RESULTS AND DISCUSSION

The reactivity ratios of the monomers (r_1 for methacrylates and r_2 for TAC) were determined according to Fineman–Ross (F–R)¹⁰ and Kelen–Tüdös (K–T) methods in which three ways of calculation were used: graphical method (I),¹¹ graphical method regarding weight conversion (II),¹² and the least-squares technique¹³ (III). As shown in Tables II to VII, the rate polymerization of TAC with methacrylates is a function of both the concentration of monomers and the size of alkyl group in methacrylates. For the systems PrMA–TAC, PtMA–TAC, and HxMA–TAC, a higher rate of polymerization was observed on increasing content of methacrylates in the feed, while for the systems of HpMA–TAC, OcMA–TAC, and DdMA–TAC, the similar rate-

Table II Experimental Data for Copolymerization of Propyl Methacrylate (M_1) with Triallyl Cyanurate (M_2) at 60 ± 1°C in Presence of Benzoyl Peroxide (0.3% by weight)

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of TAC in Copolymer (mol %)
M_1	M_2					
90	10	0.66	5.03	7.62	0.35	1.08
80	20	0.73	5.40	7.37	0.80	2.50
70	30	0.82	8.07	9.89	1.40	4.45
60	40	0.92	3.65	3.98	1.90	6.31
50	50	1.00	5.32	5.32	2.70	9.11
40	60	1.08	4.09	3.78	3.75	14.97
30	70	1.17	4.83	4.14	5.35	19.52
20	80	1.33	4.71	3.53	7.60	29.95
10	90	1.50	4.00	2.66	11.50	52.16

Table III Experimental Data for Copolymerization of Pentyl Methacrylate (M_1) with Triallyl Cyanurate (M_2) at $60 \pm 1^\circ\text{C}$ in Presence of Benzoyl Peroxide (0.5% by weight)

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of TAC in Copolymer (mol %)
M_1	M_2					
90	10	2.25	7.15	3.18	0.30	1.12
80	20	2.33	6.09	2.61	0.70	2.64
70	30	2.37	4.54	1.92	1.09	4.15
60	40	2.50	4.26	1.70	1.52	5.84
50	50	2.58	2.65	1.03	1.98	7.69
40	60	2.67	3.50	1.31	2.65	10.46
30	70	2.75	3.05	1.11	4.23	17.34
20	80	2.92	4.89	1.67	6.71	29.27
10	90	3.25	3.24	1.00	9.71	45.91

monomer composition relationship is reversed. The reactivity of comonomers as well as the rate of polymerization may depend on steric factors and on the polarity of molecules. It appears that a purely steric effect is operative in this case because the reactivity of growing macroradical due to the inductive effect from alkyl groups cannot be significant. Triallyl cyanurate copolymerizes with methacrylates to a crosslinked network. In the present investigations no gelation, however, was found to occur at the conversion below 10%. Although branched and internally cyclized molecules were formed in the reaction,²⁰ we did not consider these

features. The reactivity of all three allyl groups was assumed to be the same and conversion independent. In fact, Dušek and Spěvaček^{21,22} show that the effect of cyclization on copolymerization reactivity ratios in a system with multivinyl monomer is insignificant.

The reactivity ratios r_1 and r_2 calculated by using F-R and K-T methods are presented in Table VIII. The values resulting from F-R and K-T methods are different, but deviations are not too large. For the three ways of calculating within the K-T method, slight differences in r_1 values and somewhat higher in r_2 , are observed. In general, however, r_1

Table IV Experimental Data for Copolymerization of Hexyl Methacrylate (M_1) with Triallyl Cyanurate (M_2) at $60 \pm 1^\circ\text{C}$ in Presence of Benzoyl Peroxide (0.5% by weight)

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of TAC in Copolymer (mol %)
M_1	M_2					
90	10	3.58	5.24	1.46	0.25	1.02
80	20	3.50	6.24	1.78	0.62	2.54
70	30	3.15	6.73	2.14	1.11	4.59
60	40	2.83	5.36	1.89	1.55	6.46
50	50	3.00	3.91	1.30	2.12	8.94
40	60	4.25	2.85	0.67	2.64	11.24
30	70	3.55	2.68	0.75	3.28	14.15
20	80	4.22	2.52	0.57	4.95	20.09
10	90	4.95	4.41	0.89	9.25	45.33

Table V Experimental Data for Copolymerization of Heptyl Methacrylate (M_1) with Triallyl Cyanurate (M_2) at $60 \pm 1^\circ\text{C}$ in Presence of Benzoyl Peroxide (0.5% by weight)

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of TAC in Copolymer (mol %)
M_1	M_2					
90	10	6.60	7.52	1.14	0.28	1.14
80	20	5.27	7.79	1.47	0.58	2.57
70	30	4.23	7.78	1.84	0.95	4.23
60	40	3.15	6.59	2.09	1.35	6.05
50	50	2.83	6.54	2.31	1.82	8.21
40	60	2.30	7.88	3.43	2.40	10.93
30	70	1.95	4.99	2.56	3.22	14.86
20	80	1.65	3.16	1.92	4.72	22.33
10	90	2.77	6.16	2.22	9.05	46.14

values obtained from F-R and K-T graphical method are consistent. Bigger differences were found for r_2 values as well as for both r_1 and r_2 ones for the systems OcMA-TAC and DdMA-TAC. Figure 1 shows a η versus ξ plot for all copolymerization systems according to the graphical K-T method. From the results presented in Table VIII, it is interesting to note that the length of the alkyl group in a methacrylate exerts certain influence on the reactivity ratios of monomers. The values of reactivity ratios r_1 for PrMA, PtMA, HxMA, and HpMA are large and only differ slightly from one another, while for OcMA and DdMA the values are considerably smaller. The reactivity of allyl esters with the

majority of reactive monomers is relatively small.¹ We found this in the present investigations, too. The values of r_2 for TAC are very small and almost the same for all systems. Knowledge of reactivity ratios allows us to predict the structure of the copolymer. For all the systems the values of r_1 are greater than 1 and r_2 less than 1. This means that both radicals prefer methacrylates, and copolymers are enriched in methacrylate units. The product of the reactivity ratios indicates that the two monomers have the tendency to alternate (Table VIII). Figure 2 shows the plots of molar fraction of TAC in the copolymer (m_2) as a function molar fraction of TAC in monomer feed (M_2). For all copolymers the composition

Table VI Experimental Data for Copolymerization of Octyl Methacrylate (M_1) with Triallyl Cyanurate (M_2) at $60 \pm 1^\circ\text{C}$ in Presence of Benzoyl Peroxide (0.5% by weight)

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of TAC in Copolymer (mol %)
M_1	M_2					
90	10	6.13	7.09	1.17	0.33	1.56
80	20	4.67	5.65	1.21	0.61	2.90
70	30	4.33	5.73	1.32	1.13	5.40
60	40	2.92	5.00	1.71	1.60	7.69
50	50	2.25	7.55	3.36	2.26	10.96
40	60	1.58	5.56	3.51	3.07	15.05
30	70	1.50	6.95	4.63	4.01	19.84
20	80	1.67	4.30	2.58	5.47	27.63
10	90	1.58	5.10	3.22	7.92	41.32

Table VII Experimental Data for Copolymerization of Dodecyl Methacrylate (M_1) with Triallyl Cyanurate (M_2) at $60 \pm 1^\circ\text{C}$ in Presence of Benzoyl Peroxide (0.5% by weight)

Composition of Starting Mixture (mol %)		Polymerization Time (h)	Conversion (wt %)	Polymerization Rate (wt %/h)	N Content in Copolymer (wt %)	Fraction of TAC in Copolymer (mol %)
M_1	M_2					
90	10	4.83	4.60	0.95	0.30	1.82
80	20	4.75	5.00	1.05	0.66	3.99
70	30	3.75	10.00	2.67	0.98	5.93
60	40	2.83	2.32	0.82	1.33	8.06
50	50	2.33	9.25	3.97	1.80	10.87
40	60	1.67	10.30	6.18	2.19	13.20
30	70	1.42	5.19	3.65	2.73	16.49
20	80	1.67	4.51	3.87	4.13	24.89
10	90	1.50	8.50	5.67	7.29	43.17

curves are similar. The reactivity of methacrylates is high (including OcMA and DdMA). It causes a rapid change in the composition of the monomer feed. The relatively low rate of conversion of TAC,

even at the initial mole fraction of TAC as high as 90%, is consistent with the low values of r_2 .

Table VIII contains also the Alfrey-Price copolymerization parameters Q_1 and e_1 for methacrylates.

Table VIII Reactivity Ratios of Alkyl Methacrylates (M_1) with Triallyl Cyanurate (M_2) and Q_1 and e_1 Values for Methacrylates

Monomers	r	Fineman-Ross Method	Kelen-Tüdös Method			Q_1	e_1
			I	II	III		
PrMA-TAC	r_1	30.65	30.54	30.84	29.946	0.41	0.15
	r_2	-0.042 ^a	0.037	0.032	0.031		
	$r_1 \cdot r_2$	—	—	—	0.9283		
PtMA-TAC	r_1	29.52	29.46	29.55	31.159	0.47	0.39
	r_2	-0.021 ^a	0.0262	0.0236	0.0269		
	$r_1 \cdot r_2$	—	—	—	0.8113		
HxMA-TAC	r_1	28.17	28.29	28.41	28.982	0.47	0.42
	r_2	0.018	0.005	0.005	0.0258		
	$r_1 \cdot r_2$	—	—	—	0.7472		
HpMA-TAC	r_1	27.92	27.96	28.03	28.419	0.45	0.38
	r_2	0.023	0.029	0.021	0.0274		
	$r_1 \cdot r_2$	—	—	—	0.7787		
OcMA-TAC	r_1	21.99	22.50	22.51	22.932	0.52	0.69
	r_2	0.060	0.015	0.050	0.0223		
	$r_1 \cdot r_2$	—	—	—	0.5114		
DdMA-TAC	r_1	17.19	18.40	18.90	18.392	0.25	0.13
	r_2	0.033	0.058	0.067	0.051		
	$r_1 \cdot r_2$	—	—	—	0.9380		

^a $r_2 < 0$ attributable to experimental error. For TAC $Q_2 = 0.013$ and $e_2 = -0.12$.²³

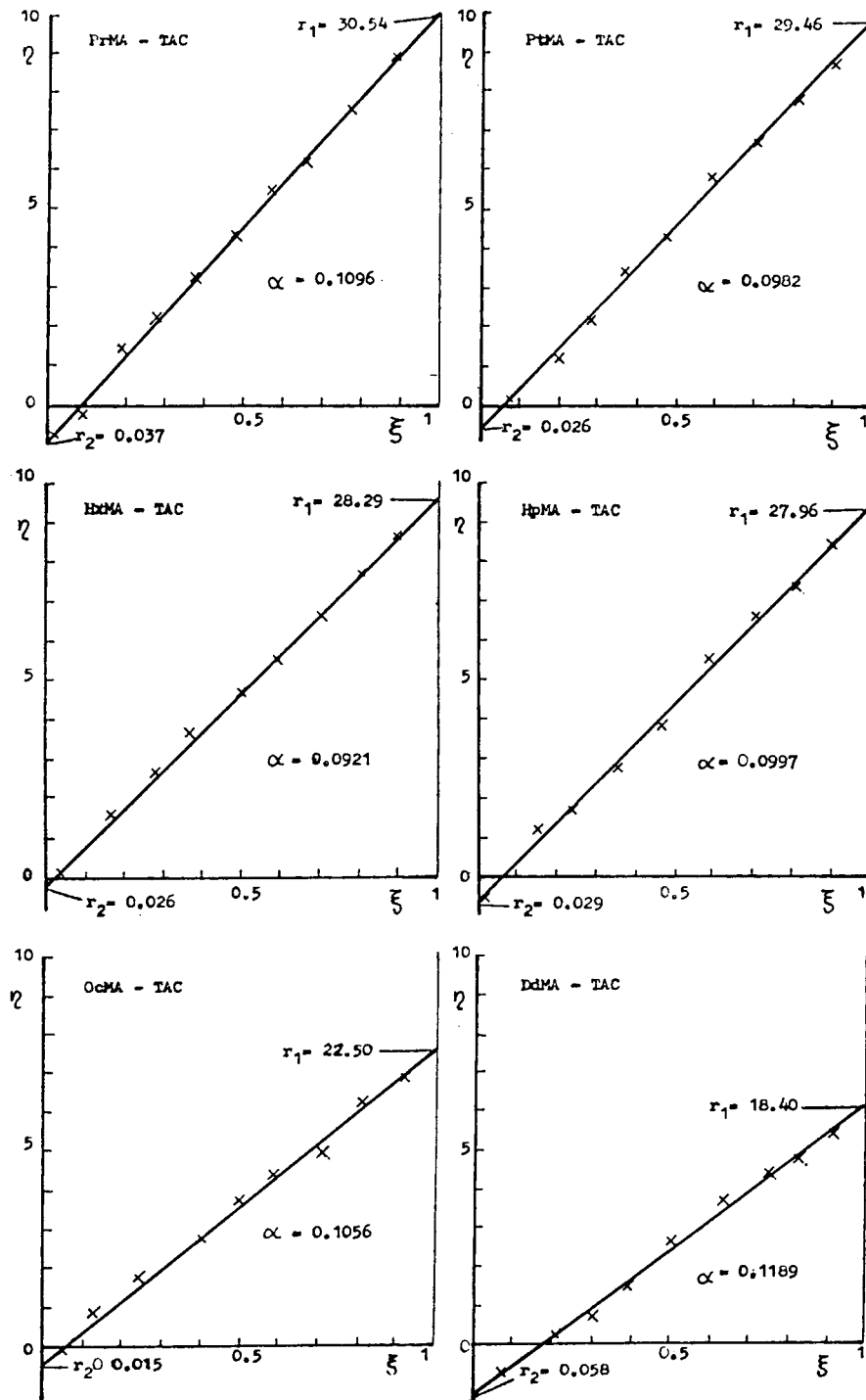


Figure 1 The η versus ξ plot for systems of alkyl methacrylates with triallyl cyanurate. The Kelen-Tüdös graphical method, where $r_1/3 = \eta$ and $-3r_2/\alpha = \eta$.

These values were calculated from the reactivity ratios r_1 and r_2 obtained by the K-T method using the least-squares technique and from literature for Q_2 and e_2 for TAC ($Q_2 = 0.013$, $e_2 = -0.12$).²³ The calculated values of Q_1 (Table VIII) are not so large

and do not differ significantly from one another, with one exception for the DdMA-TAC system, where Q_1 is slightly smaller. The values e_1 for methacrylates also differ slightly from those obtained by other authors.²³⁻²⁵

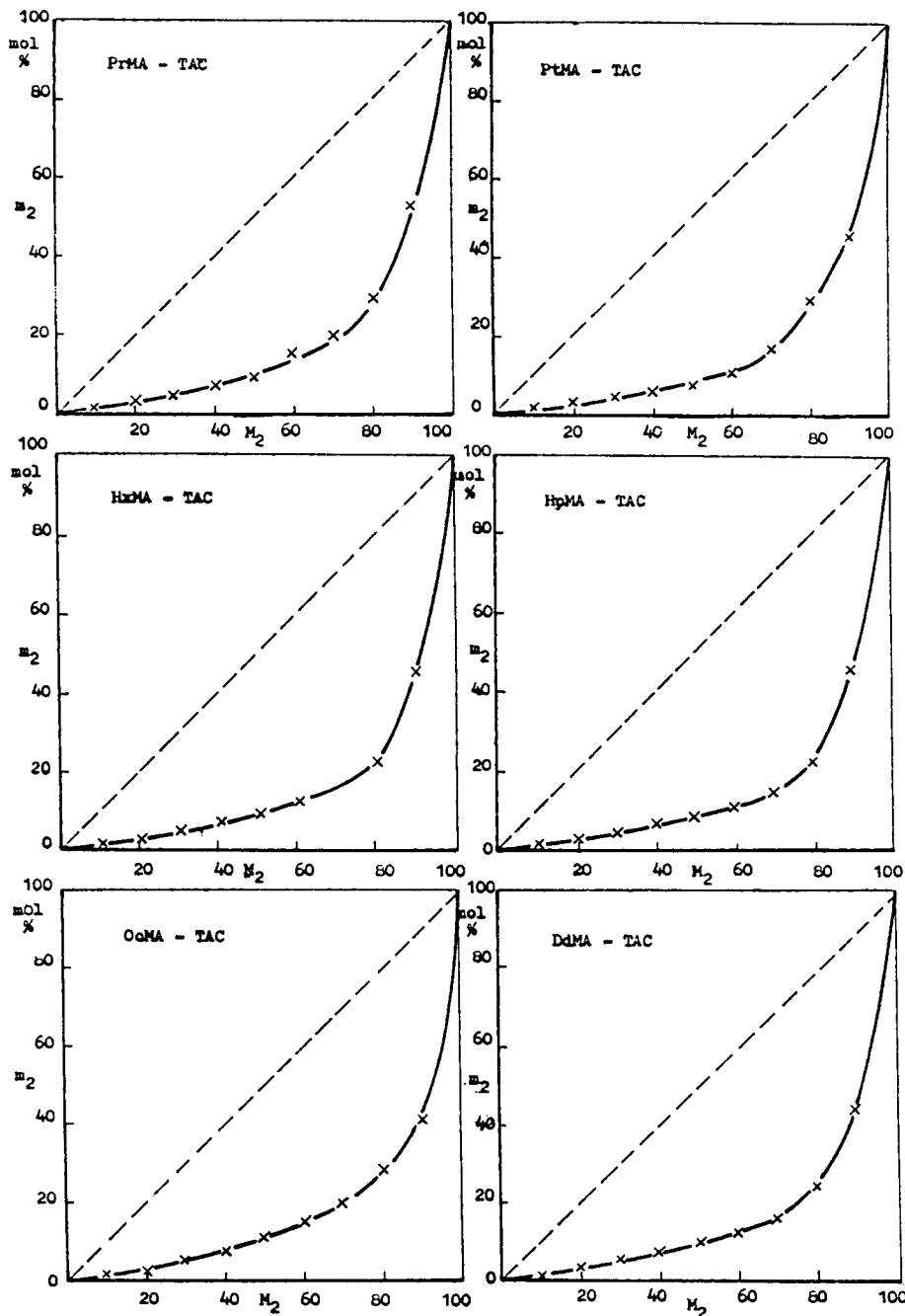


Figure 2 Relationship of the molar fraction of TAC in the feed (M_2) and the molar fraction in the copolymer (m_2).

REFERENCES

1. W. R. Roth and R. F. Church, *J. Polym. Sci.*, **55**, 41-48 (1961).
2. M. Kucharski and A. Rytzel, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 3011-3013 (1978).
3. M. Kucharski and A. Rytzel, *Polymer*, **25**, 555-558 (1984).
4. M. Kucharski and A. Rytzel, *Polimery*, **26** (10), 381-384 (1981).
5. G. Van Paesschen and D. Timmerman, *Macromol. Chem.*, **74**, 112 (1964).
6. A. Rytzel, *Acta Polymerica*, **41** (5), 289-293 (1990).
7. J. Pielichowski, et al., *Termochimica Acta*, **94**, 367-378 (1985).
8. *Encyclopedie Polym. Sci. Tech.*, Wiley, New York, 1971, Vol. 4, p. 659.

9. A. Rytzel, *Acta Polymerica*, **40**(11), 690-694 (1989).
10. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259-265 (1950).
11. T. Kelen and F. Tüdös, *Reaction, Kinetics Catalysis Lett.*, **1**(4), 487-492 (1974).
12. F. Tüdös, et al., *Reaction Kinetics Catalysis Lett.*, **2**(4), 439-447 (1975).
13. T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem.*, **A9**, 1-27 (1975).
14. P. R. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
15. R. Hill, U. S. Pat. 2,129,690 (1938).
16. H. J. Barnet and D. E. Stain, U. S. Pat. 2,129,666 (1938).
17. A. Rytzel, *Zeszyty Naukowe Politechniki Rzeszowskiej* (41), Chemia 3, Rzeszów (1989).
18. *Preparatyka Tworzyw Sztucznych*, Warszawa, PWT, 1961.
19. B. Bobrański, *Analiza Ilościowa Związków Organicznych*, Warszawa, PWN, 1956.
20. J. K. Gillham and C. C. Mentzer, *Polym. Preprints*, **13**, 247 (1972).
21. K. Dušek and J. Spěvaček, *Polymer*, **21**, 750-756 (1980).
22. K. Dušek, "Network Formation by Chain Crosslinking (Co) Polymerization," in "*Developments in Polymerization*," R. N. Haward, Ed., App. Sci. Publ. Ltd., Barking, 1982, Vol. 3, pp. 143-206.
23. R. Z. Greenley, *J. Macromol. Sci.-Chem.*, **A9**(4), 505-516 (1975).
24. E. C. Leonard, *Vinyl and Diene Monomers, Part I*, Wiley, New York, 1970 p. 189.
25. J. K. Borchardt and E. Dwyan Dalrymple, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1754-1764 (1982).

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