Wojtczak, Czerniawski and Rozwadowska: Copolymerization of
acrylonitrile with some transition metal acrylates. I

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125

Kurze Mitteilungen

Copolymerization of acrylonitrile with some transition metal acrylates

I. Determination of monomer reactivity ratios in radical copolymerization of acrylonitrile with zinc acrylate in dimethylformamide

1. Introduction

Vinyl polar monomers such as acrylonitrile, methacrylonitrile or methyl methacrylate can copolymerize in the presence of Lewis acid with some non-polar monomers, e.g. styrene resulting in alternating copolymers [1—4]. In electron donor solvent or in the absence of Lewis acid they copolymerize too, but random copolymers are obtained. The difference in the behaviour of these monomers results from changes in electron density in the vinyl group of monomers coordinated with metal ions as well those bound in a charge-transfer ternary complex [5, 6].

In dimethylformamide solution of zinc acrylate the coordination of acrylonitrile with zinc ions is not observed and random copolymerization takes place. The present paper deals with the determination of monomer reactivity ratios in this system.

2. Experimental

2.1. Materials

Acrylic acid (AA), acrylonitrile (AN), dimethylformamide (DMF) and methanol, all commercial grade, were purified according to standard procedures. Azobisisobutyronitrile (AIBN) — International Enzymes Ltd., Windsor, England, was purified by crystallization from methanol. Zinc oxide p.a. was used without further purification. Zinc acrylate (ZnA$_2$) obtained in the reaction of ZnO and AA in toluene suspension at 40 to 50 °C was dried at 50 °C in vacuo [7, 8].

2.2. Synthesis

Copolymerization of acrylonitrile, M$_1$, with zinc acrylate, M$_2$, was performed at 60 °C in DMF solution with AIBN as an initiator in an atmosphere of nitrogen. The total amount of monomers was 4 mol/l in series A and B and 1 mol/l in series C. The amount of initiator was $9 \cdot 10^{-3}$ mol/l. After a given period of time the copolymer solution was poured into a large excess

of cold methanol. The precipitated copolymers were purified by repeated extraction with methanol and then dried at 50 °C in vacuo. The copolymer compositions were determined by nitrogen and Zn metal analysis.

3. Results and discussion

It was observed that the copolymerization of acrylonitrile with zinc acrylate in DMF occurs in a homogeneous phase provided that monomer mixtures contain less than 12 mole-% of ZnA$_2$. The data concerning copolymerization systems under study are summarized in Table 1. $F = M_1/M_2$ is the initial mole ratio of monomer mixtures and $f = m_1/m_2$ is the mole ratio of mers in the copolymers. M_2 denotes twice molar concentration of ZnA$_2$, similarly as for symmetrical divinyl monomers [9, 10]. The conversion data of series A suggest that the greater the mole fraction of ZnA$_2$ in feed the higher the rate of copolymerization.

For the determination of reactivity ratios the Kelen-Tüdős methods [11, 22] were used. From the straight lines shown in Fig. 1 it can be supposed that conventional copolymer composition equation is adequate for the experimental data. However, under such conditions a precise value of reactivity ratio can be calculated only for the comonomer which is in very large excess. Because of high value of α the other reactivity ratio can not be estimated with the same precision.

For comparative purposes an approximate method [13, 14] for calculation of r_1 was used:

$$r_1 = \lim_{1/F \to 0} (f/F).$$

The plot of $1/F$ versus f/F is given in Fig. 2, and r_1 can be compared in Table 2. It is seen that the KT methods, both for low conversion and for high conversion (cf. Table 1) as well as the third method (GP) give the same result within the limits of error. For the determination of r_2 the copolymerizations of acrylonitrile with a very large excess of ZnA$_2$ were performed (series C). The respecting plot and a value of r_2 are shown in Fig. 1 and Table 2, respectively.

Table 1. Copolymerization of AN with ZnA$_2$. Composition conversion data obtained at 60 °C in DMF with AIBN as initiator

Run	M_2	F	Polymerization time min	Conversion wt. %	m_2	f
A1	0.514	193.6		18.14	1.073	92.15
A2	1.033	95.80	60	10.22	2.256	43.32
A3	2.092	46.80	35	10.52	4.413	21.66
A4	5.377	17.60	30	11.79	10.32	8.689
A5	8.274	11.24	30	12.67	14.38	5.952
A6	11.34	7.82	30	20.99	17.31	4.777
B1	2.621	37.15	30	8.51	5.559	16.99
B2	4.138	23.16	18	2.19	8.340	10.76
B3	5.769	15.29	20	7.11	11.97	7.354
B4	9.233	9.831	15	4.66	16.08	5.219
B5	10.23	8.776	12	3.35	17.23	4.802
C1	76.05	0.3150	[1])	3.17	63.30	0.5799
C2	81.77	0.2229		3.03	66.77	0.4977
C3	86.06	0.1620		4.23	70.51	0.4183
C4	90.53	0.1046	≈5	3.72	76.73	0.3032

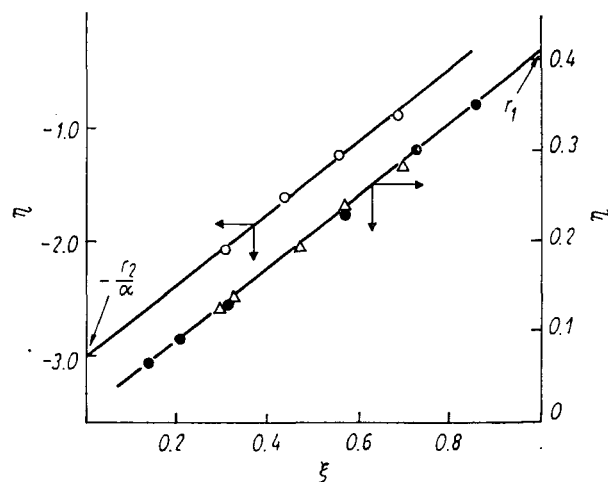[1]) Polymerization time in serie C was not precise determined

Fig. 1. Kelen-Tüdős plot for copolymerization of acrylonitrile with zinc acrylate in DMF at 60 °C: ● — series A, △ — series B, ○ — series C; $\alpha_A = 88.59$, $\alpha_B = 36.10$, $\alpha_C = 0.0786$
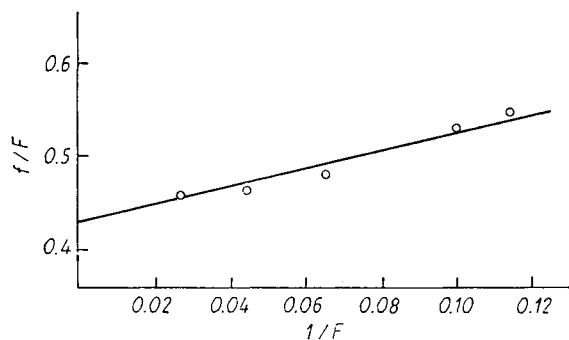
Fig. 2. Plot of f/F vs. $1/F$ for acrylonitrile — zinc acrylate
copolymer to determine r_1, series B

Table 2. Reactivity ratios for the copolymerization of AN (1)
with ZnA_2 (2)

Series	Method	r_1 (AN)	r_2 (ZnA$_2$)
A	KT extended	0.41 ± 0.02	—
B	KT	0.41 ± 0.02	—
	GP	0.43 ± 0.02	—
C	KT	—	0.24 ± 0.03

The results of copolymerization of some other transition
metal acrylates with acrylonitrile will be discussed in a later
paper.

Summary

Copolymerization of acrylonitrile with Zn salt of acrylic
acid has been studied in dimethylformamide solution at 60 °C
with AIBN as an initiator. Reactivity ratios have been calculated
by the methods due to KELEN-TÜDÖS and GHOSH-PALIT.

The rate of copolymerization increases with the growth of mole
fraction of zinc acrylate in feed. The system has the following
reactivity ratios (AN as monomer 1): $r_1 = 0.41$, $r_2 = 0.24$.

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Z. WOJTCZAK, T. CZERNIAWSKI and
B. ROZWADOWSKA
Institute of Chemistry,
N. Copernicus University,
87-100 Toruń, Poland

Zur Beeinflussung der Struktur von Schnellspinnseide aus Polyethylenterephthalat durch Zusätze von Polybutylenterephthalat

1. Einleitung

Neben der chemischen Struktur ist für die Eigenschaften
von Schnellspinnseide aus Polyethylenterephthalat dessen
geringe Kristallisationsgeschwindigkeit bestimmend. Erst ober-
halb einer Spinngeschwindigkeit von 3000 m/min setzt eine
durch die Orientierung initiierte Kristallisation ein [1]. In
Abhängigkeit von der Spinngeschwindigkeit ist eine Trennung
der schnell verlaufenden Orientierungsvorgänge von den
Kristallisationsprozessen im PETP-Faden möglich. Hierauf
beruhen die bei niedrigen Geschwindigkeiten erzielten hohen
Thermo-Schrumpfwerte der PETP-Seiden. Wir gingen von der
Annahme aus, daß durch Zusatz des von der Spritzgießver-
arbeitung her bekannten Polybutylenterephthalats (PBTP)
mit raschem Kristallisationsablauf [2] das Kristallisations-
verhalten der Polymermischung positiv beeinflußt werden
müßte.

2. Experimentelles

2.1. Durchführung der Spinnversuche

Mit Hilfe der einstelligen Labor-Spinnanlage des Institutes
für Technologie der Fasern in Dresden wurde PETP-Schnell-
spinnseide im Geschwindigkeitsbereich von 2000 bis 5000
m/min mit Zumischungen von 0 bis 100% PBTP ersponnen.
Der Durchsatz betrug 30 g/min; die Spinntemperaturen wurden
im Hinblick auf das vom PETP abweichende Temperatur-
Viskositäts-Verhalten des PBTP variiert.

2.2. Strukturphysikalische Untersuchungen an den Fäden

2.2.1. Untersuchung des Kristallisationsverhaltens

Für die Messungen des Kristallinitätsgrades wurde ein
Differential-Scanning-Calorimeter vom Typ DSC-2 (Perkin-
Elmer) verwendet. Folgende Aufnahmebedingungen wurden
gewählt[1]:

Einwaage: 5 mg Seide;
Empfindlichkeit: 20,9 mJ s^{-1} (5 mcal s^{-1});
Aufheizgeschwindigkeit: 20 K/min;
N_2 — Atmosphäre.

Die anhand einer Auswertung der Meßkurven erhaltenen
Ergebnisse sind in Tabelle 1 angeführt; darin bedeuten

m_{PETP}: Masseanteil PETP im Spinnpolymer in %;
m_{PBTP}: Masseanteil PBTP im Spinnpolymer in %;
v: Spinngeschwindigkeit in m · min^{-1};
T^{SL}: Schmelztemperaturen des PETP und des PBTP in K;
ΔH^{SL}: Schmelzenthalpien des PETP und des PBTP in Jg^{-1};
α: Kristallinitätsgrad des PETP und des PBTP in %,
bezogen auf den Anteil der jeweiligen Komponente
im Spinnpolymer;
T^{Kr}_{PETP}: Kristallisationstemperatur des PETP in K;
ΔH^{Kr}_{PETP}: Kristallisationsenthalpie des PETP in Jg^{-1}.

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[1] Für die Durchführung der Messungen danken wir Frau
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