DEVELOPMENT OF SCIENCE

ISNN 3030-3907

2026 AUGUST

ISSUE - 8
VOLUME -1

DEVELOPMENT OF SCIENCE

D E V O S

РАЗВИТИЕ НАУКИ

ILM-FAN TARAQQIYOTI

Development of science

Scientific journal
Ilmiy jurnal
Научный журнал

AUGUST 2026
Issue - 8, VOLUME - 1

ISSN 3030 -3907

*The scientific journal **«Development of Science»** was registered by the State on April 15, 2024 with certificate number №256445.*

***«Ilm fan tarqqiyoti»** ilmiy jurnali 2024 yil 15 aprel kuni №256445 sonli guvohnoma bilan Davlat ro'yxatidan o'tgan.*

*Научный журнал **«Развитие науки»** был зарегистрирован государством 15 апреля 2024 года под номером свидетельства № 256445.*

The proceedings will be provided to the authors in electronic form (PDF format). The authors bear full responsibility for the content of the articles included in the proceedings, the accuracy and reliability of the statistical data and regulatory documents cited therein, as well as for any opinions and judgments expressed in their articles. Articles that do not meet the established requirements will not be included in the proceedings. The Organizing Committee reserves the right to shorten the text of an article, make minor editorial corrections, and assign submissions to the appropriate sections.

To'plam elektron ko'rinishda (pdf formatida) mualliflarga taqdim etiladi. To'plamga kiritiladigan maqolalarning mazmuni, ulardagi statistik ma'lumotlar va me'yoriy hujjatlarning to'g'riligiga hamda har qanday fikr - mulohazalarga mualliflarning o'zlari mas'ul hisoblanadilar.Talablarga javob bermaydigan maqolalar to'plamga kiritilmaydi. Tashkiliy qo'mita maqola matnini qisqartirish, qisman tuzatish kiritish, seksiyalarga joylashtirish huquqiga ega.

Сборник предоставляется авторам в электронном виде (в формате PDF). Авторы несут полную ответственность за содержание статей, включённых в сборник, достоверность приведённых в них статистических данных и нормативных документов, а также за изложенные мнения и суждения. Статьи, не соответствующие установленным требованиям, в сборник не включаются. Организационный комитет оставляет за собой право сокращать текст статьи, вносить отдельные редакционные исправления и распределять материалы по соответствующим секциям.

EDITOR-IN-CHIEF:
Temirov Alisher Hashim oglu - Doctor of Philosophy (PhD) in Technical Sciences, Associate Professor.
CHAIRMAN OF THE EDITORIAL BOARD:
Fozilov Sadriddin Fayzullayevich - Doctor of Technical Sciences, Professor
MEMBERS OF THE EDITORIAL BOARD:

Faheem Uddin
Professor,Iqra university, Pakistan
Siddikova Sadokat Gafforovna
DSc, Rector of Bukhara State Technical University, Uzbekistan
Dr. Amit Rawal
Professor, Department of Textile and Fibre Engineering Indian Institute of Technology Delhi, India
Alexander Vitalievich Dudan
Associate Professor, Euphrosyne Polotskaya State University of Polotsk, Republic of Belarus
Bozorov Gayrat Rashidovich
Professor Bukhara State Technical University, Uzbekistan
Vladimir Mikhailovich Kapustin
Professor,Gubkin Russian State University of Oil and Gas (National Research University),Russian Federation
Shaoliang Chen
Ph. D., Engineer,Cement Science and New Building Materials Research Institute, China
Tukhtayeva Zebo Sharifovna
Bukhara State Technical University, Professor.
Kodirov Abduakhad Abdurakhimovich
Karshi State University, Professor
Turemuratov Sharibay Naurizbaevich
General Scientific Secretary of the Karakalpakstan Branch of the Academy of Sciences of the Republic of Uzbekistan, Professor
Tursunov Kakhor Shonazarovich
Karshi State University, Professor
Sharipov Muzaffar Samandarovich
Bukhara State University, Professor.
Alikulov Rustam Valiyevich
Termez State University, Professor
Makhmudov Mukhtar Jamolovich
Bukhara State Technical University, Professor.
Oral Kurganbekovich Beyseynbayev
Professor,M. Auezov South Kazakhstan University,Republic of Kazakhstan
Tropov Khamza Tursunovich
Samarkand State University, Professor
Nizamov Aslitdin Badreddinovich
Bukhara State Technical University, Professor.
Saidakhmedova Nodira Ilkhomovna
Tashkent State University of Economics, Professor

ORGANIZATIONAL STRUCTURE:

Safarov J.A.-*editor*
Panoyev N.Sh. -*editor*
Buranov N.G. -*assistant editor*
Shodiyev D.X.- *layout editor*
Izzatov D.X. - *layout editor*
Urinov J.B. - *layout editor*
Temirov A.T. - *graphic designer*
Temirov I.G. – *layout designer*

Changes to the composition of the Editorial Board, including the appointment of new members or the removal of existing members, shall be made by the Editor-in-Chief.

www.devos.uz

ISSN 3030-3907

UDK: 678.01:541.124

MODELING OF TERPOLYMERIZATION KINETICS AND DETERMINATION OF REACTIVITY RATIOS IN THE TDMA–STYRENE–MALEIC ANHYDRIDE SYSTEM

Mavlonov Shohrux Boboxon ogli

Doctor of Philosophy (PhD) in Technical Sciences, Associate Professor, Department of Chemical Technology, Bukhara State Technical University, Bukhara, Republic of Uzbekistan; E-mail: shoxrux-mavlonov@mail.ru

https://orcid.org/0009-0009-1652-6369, Science ID: FBX-0325-0012

Fozilov Sadriddin Fayzullayevich

Doctor of Science, Professor, Academician of the Academy of Sciences of the Republic of Uzbekistan, Professor of the Department of Chemical Technology, Bukhara State Technical University, Bukhara, Republic of Uzbekistan: https://orcid.org/0009-0009-0313-6134, Science ID: DBX-0326-0003

Abstract. In this study, the kinetics of terpolymerization, compositional evolution, and monomer reactivity ratios in the TDMA–styrene–maleic anhydride system were comprehensively investigated. Increasing the initiator concentration from 16.8×10^{-6} to 51.3×10^{-6} mol•L^{-1} led to an increase in conversion from 6.4% to 15.2% and reaction rate from 4.075×10^{-6} to 8.965×10^{-6} mol•L^{-1}•s^{-1}. At low conversion (Xw≈0.02–0.09), the terpolymer composition remained close to the initial feed, although deviations due to differences in monomer reactivity were observed. With increasing conversion, some systems exhibited stable composition (±0.02), while others showed compositional drift (increase of MA fraction from 0.50 to 0.70). The determined reactivity ratios (rTDMA/St≈0.99; rSt/TDMA≈1.62; rTDMA/MA≈2.02; rMA/TDMA≈0.34; rSt/MA≈1.50; rMA/St≈0.32) indicate the dominant incorporation of TDMA and styrene and selective incorporation of MA. The ternary kinetic model demonstrated high agreement with experimental data (±0.03).

Keywords: TDMA, styrene, maleic anhydride, terpolymerization, radical polymerization, kinetics, compositional drift, reactivity ratios, kinetic modeling, ternary system, donor–acceptor mechanism, molecular weight, polydispersity, functional polymers.

Anatatsiya. Ushbu tadqiqotda TDMA–stirol–malein angidrid uch monomerli sistemasida terpolimerlanish kinetikasi, tarkibiy o`zgarishlari va monomerlarning reaktivlik nisbatlari kompleks o‘rganildi. Inisiator konsentratsiyasi $16,8\times10^{-6}$ dan $51,3\times10^{-6}$ mol·L^{-1} gacha oshirilganda konversiya 6,4 % dan 15,2 % gacha, reaksion tezlik $4,075\times10^{-6}$ dan $8,965\times10^{-6}$ mol·L^{-1}·s^{-1} gacha ortdi. Past konversiyada (Xw≈0,02–0,09) tarkib boshlang‘ich qiymatlarga yaqin bo‘ldi, ammo reaktivlik farqlari sabab og‘ishlar kuzatildi. Konversiya ortishi bilan ayrim uch monomerli sistemalarda tarkib barqaror (±0,02),

boshqalarida esa kompozitsion drift (MA 0,50–0,70 gacha ortishi) aniqlandi. Reaktivlik nisbatlari ($r_{TDMA/St}$≈0,99; $r_{St/TDMA}$≈1,62; $r_{TDMA/MA}$≈2,02; $r_{MA/TDMA}$≈0,34; $r_{St/MA}$≈1,50; rMA/St≈0,32) TDMA va stirolning ustun, MA ning selektiv inkorporatsiyasini ko‘rsatdi. Uch komponentli model eksperimental natijalar bilan yuqori moslik (±0,03) namoyon etdi.

Kalit so`zlar: TDMA, stirol, malein angidrid, terpolimerlanish, radikal polimerlanish, kinetika, kompozitsion drift, reaktivlik nisbatlari, kinetik modellashtirish, uch monomerli sistema, donor–akseptor mexanizmi, molekulyar massa, polidisperslik, funksional polimerlar.

Аннотация: В данной работе комплексно исследованы кинетика терполимеризации, составные изменения и реакционные способности мономеров в системе TDMA–стирол–малеиновый ангидрид. При увеличении концентрации инициатора от $16{,}8\times10^{-6}$ до $51{,}3\times10^{-6}$ моль•л$^{-1}$ конверсия возрастает с 6,4 % до 15,2 %, а скорость реакции — с $4{,}075\times10^{-6}$ до $8{,}965\times10^{-6}$ моль•л$^{-1}$•с$^{-1}$. В области низких конверсий (X_w≈0,02–0,09) состав терполимера близок к исходному, однако наблюдаются отклонения, обусловленные различиями реакционной способности мономеров. С ростом конверсии в одних системах состав остается стабильным (±0,02), в других наблюдается композиционный дрейф (увеличение доли MA с 0,50 до 0,70). Определённые реакционные коэффициенты ($r_{TDMA/St}$≈0,99; $r_{St/TDMA}$≈1,62; rTDMA/MA≈2,02; rMA/TDMA≈0,34; rSt/MA≈1,50; $r_{MA/St}$≈0,32) свидетельствуют о преобладающем включении TDMA и стирола и селективной инкорпорации MA. Трёхкомпонентная модель показала высокое соответствие экспериментальным данным (±0,03).

Ключевые слова: TDMA, стирол, малеиновый ангидрид, терполимеризация, радикальная полимеризация, кинетика, композиционный дрейф, реакционные коэффициенты, кинетическое моделирование, трёхкомпонентная система, донорно-акцепторный механизм, молекулярная масса, полидисперсность, функциональные полимеры.

INTRODUCTION

Currently, the demand for highly efficient functional additives in the petrochemical industry, as well as in fuel and lubricant production, is rapidly increasing [1,2]. In particular, polymer-based modifiers that enhance rheological, thermal, and low-temperature properties are of great importance for fuels operating under severe conditions. In this context, terpolymers based on long-chain alkyl methacrylates, aromatic vinyl monomers, and functional anhydrides are considered

ISSN 3030-3907

promising additives [3,4]. Ternary systems based on TDMA (tetradecyl methacrylate), styrene, and maleic anhydride are distinguished by their structural diversity, the presence of functional groups, and the ability to control chain formation [5,6]. The terpolymers obtained in such systems can exhibit a high viscosity index, good dispersing properties, and improved low-temperature performance. Therefore, a detailed study and theoretical modeling of the kinetics of TDMA–St–MA terpolymerization are of significant scientific and practical importance [7].

Radical copolymerization and terpolymerization processes have been extensively studied in the literature and are primarily based on monomer reactivity ratios, as well as chain growth and termination mechanisms. Classical methods such as the Mayo–Lewis and Fineman–Ross equations have been developed to determine reactivity ratios for binary systems [8,9]. The styrene–maleic anhydride system is well known as a donor–acceptor pair and typically forms alternating copolymers [10,11]. However, systems involving long-chain alkyl methacrylates (including TDMA) have not been sufficiently investigated with respect to diffusion limitations, gel effect, and enhanced chain transfer reactions. In recent years, kinetic modeling of multicomponent systems has increasingly employed advanced approaches such as PREDICI simulations, Monte Carlo methods, and deterministic kinetic models[12]. These approaches enable the prediction of monomer conversion, molecular weight distribution, and structural composition [13,14].

Nevertheless, in existing studies, several aspects of ternary systems such as TDMA–St–MA remain insufficiently investigated. In particular, the accurate determination of reactivity ratios and their dependence on conversion, as well as the complex influence of diffusion-controlled (DC) effects on propagation and termination rate constants, have not been systematically studied. Furthermore, the kinetic parameters in the high-conversion region (50–95%) and the level of agreement between experimental data and mathematical models have not been adequately analyzed. In particular, the integration of diffusion limitations arising from the significant increase in medium viscosity due to the presence of long-chain TDMA into kinetic models, as well as their influence on terpolymer composition, has not been fully elucidated. In addition, the distribution of structural units formed as a result of monomer interactions in ternary systems and their relationship with reactivity ratios have not been sufficiently investigated.

The main objective of this study is to model the kinetics of terpolymerization in the TDMA–styrene–maleic anhydride ternary system, determine reactivity ratios, and provide a scientific basis for the influence of monomer composition and diffusion limitations on process kinetics. Accordingly, the study aims to identify the initial kinetic regularities of radical terpolymerization in the TDMA–St–MA

ISSN 3030-3907

system, analyze the time dependence of monomer conversion using both experimental data and modeling approaches, and evaluate the variation of propagation and termination rate constants as a function of conversion. Furthermore, a kinetic model incorporating diffusion limitations is developed, reactivity ratios for the ternary system are determined and their effect on terpolymer composition is assessed, the agreement between experimental results and model predictions is evaluated, and optimal synthesis conditions are established.

Research Methods and the Received Results

General experimental procedure: To investigate the kinetics of terpolymerization in the TDMA–styrene–maleic anhydride (TDMA–St–MA) ternary system and to determine the initial kinetic regularities, experiments were carried out in the low conversion range (0–15%) [15]. This region corresponds to the kinetic control regime, where diffusion limitations are minimal. The overall kinetic process can be described by the following scheme [16,17]:

Table 1

Kinetic scheme and rate constants adopted for modeling the terpolymerization of TDMA, styrene, and maleic anhydride using the PREDICI® software *(M1 – TDMA, M2 – St, M3 – MA)*

Process description	Reaction expression	Symbol	Value $L \cdot mol^{-1} \cdot s^{-1}$
Formation of active centers (initiation)			
Initiator decomposition	I → 2I•	ki, f	7,4609E-6, 0.58 (s^{-1})
First addition of TDMA monomer	I• + M1 → P1(1)•	kp1	1333.8
First addition of styrene monomer	I• + M2 → P2(1)•	kp2	33,395
First addition of MA monomer	I• + M3 → P3(1)•	kp3	683.24
Chain propagation			
Growth of TDMA radical with TDMA	P1(s)• + M1 → P1(s+1)•	kp1	1333.8
Growth of styrene radical with styrene	P2(s)• + M2 → P2(s+1)•)	kp2	33.395
Growth of MA radical with MA	P3(s)• + M3 → P3(s+1)•	kp3	683.24
Cross-propagation			

ISSN 3030-3907

TDMA radical reacting with styrene	P1(s)• + M2 → P2(s+1)•	kp12	1333.8/r12
TDMA radical reacting with MA	P1(s)• + M3 → P3(s+1)•	kp13	1333.8/r13
Styrene radical reacting with TDMA	P2(s)• + M1 → P1(s+1)•	kp21	33,395/r21
Styrene radical reacting with MA	P2(s)• + M3 → P3(s+1)•	kp23	33,395/r23
MA radical reacting with TDMA	P3(s)• + M1 → P1(s+1)•	kp31	683.24/r31
MA radical reacting with styrene	P3(s)• + M2 → P2(s+1)•	kp32	683.24/r32
Chain transfer			
Transfer to TDMA monomer			
Transfer of TDMA radical to TDMA	P1(s)• + M1 → P(s) +P1(1)•	kf1	0.1492
Transfer of TDMA radical to TDMA	P2(s)• + M1 → P(s) +P1(1)•	kf21	3.5/r21
Transfer of styrene radical to TDMA	P3(s)• + M1 → P(s) +P1(1)•	kf31	1.9321E-2/r31
Chain transfer to styrene monomer			
Chain transfer to styrene monomer	P1(s)• + M2 → P(s) +P2(1)•	kf12	0.1492/r12
Transfer of TDMA radical to styrene	P2(s)• + M2 → P(s) +P2(1)•	kf2	4.5
Transfer of MA radical to styrene	P3(s)• + M2 → P(s) +P3(1)•	kf32	1.9321E-2/r32
Chain transfer to MA monomer			
Chain transfer to MA monomer	P1(s)• + M3 → P(s) +P3(1)•	kf13	0.1492/r13
Transfer of TDMA radical to MA	P2(s)• + M3 → P(s) +P3(1)•	kf23	3.5/r23
Transfer of MA radical to MA	P3(s)• + M3 → P(s) +P3(1)•	kf3	1.9321E-2
Intramolecular chain transfer of BA			
Formation of secondary radical	P1(s)• → Q1(s)•	kbb	553
Short-chain branching			

ISSN 3030-3907

Formation of secondary radical	Q1(s)• + M1 → P1(s+1)•	kp1tert	49.401
Reaction with styrene	Q1(s)• + M2 → P2(s+1)•	kp12tert	49.401/r12
Reaction with MA	Q1(s)• + M3 → P3(s+1)•	kp13tert	49.401/r13
Degradative chain transfer			
With TDMA	Q1(s)• + M1 → P(s)+P1(1)•	kf1tert	6
With styrene	Q1(s)• + M2 → P(s)+P2(1)•	kf12tert	6/r12
With MA	Q1(s)• + M3 → P(s)+P3(1)•	kf13tert	6/r13

Materials and reagents: In the present study, tetradecyl methacrylate (TDMA) was synthesized via esterification of methacrylic acid with higher molecular weight alcohols, specifically tetradecyl alcohol. The reaction was carried out in the presence of an acid catalyst (sulfuric acid) and proceeded with the elimination of water.

$$CH_2=C(CH_3)COOH+C_{14}H_{29}OH \rightarrow CH_2=C(CH_3)COOC_{14}H_{29}+H_2O$$

Methacrylate monomers and their quality parameters in the CIS region are regulated by GOST 20370–74 (for methacrylic acid esters) or corresponding technical specifications (TU). Styrene (St) (GOST 10003–90) and maleic anhydride (MA) (GOST 11138–78) were used as monomers. An azo-type compound (IMDN) was employed as the initiator. The monomer-to-initiator ratios were selected within the range of 125:1, 200:1, and 800:1. Toluene was used as a solvent to ensure homogeneity of the reaction medium and efficient heat transfer. The monomers were studied at molar ratios of 80TDMA/10St/10MA, 10TDMA/80St/10MA, and 10TDMA/10St/80MA. All reagents used in the study were of high purity and were applied without additional purification. However, considering that monomer purity and the absence of inhibitors significantly affect polymerization kinetics, the monomers were pretreated when necessary by vacuum distillation or inhibitor removal prior to use.

The concentrations of the reactants in the overall kinetic equation are expressed as follows:

$$R_p=kp[M][R\ ]\ (1)$$

Terpolymerization process: The terpolymerization reactions were carried out under an inert atmosphere (N_2) at a temperature of 95 ± 5 °C. The reaction time was varied within the range of 0–360 minutes. Samples were withdrawn at specific

ISSN 3030-3907

time intervals, and the monomer conversion was determined. The reaction rate is described by the following general kinetic expression:

$$R_p = -\frac{d[M]}{dt} \quad (2)$$

Under steady-state conditions in radical terpolymerization:

$$[R^{\cdot}] = \sqrt{\frac{2fk_d[I]}{k_t}} \quad (3)$$

As a result, the overall rate equation is expressed as follows:

$$R_p = k_p[M] = \sqrt{\frac{2fk_d[I]}{k_t}} \quad (4)$$

Monomer conversion was calculated using the following equation:

$$ln(\frac{[M]0}{[M]}) = k_{app} \quad (5)$$

Here, $k_{app}t$ is the apparent rate constant. The linear dependence of $\ln([M]_0/[M])$ on time indicates that the process follows a pseudo-first-order kinetic model.

$$k\frac{eff}{p} = p_t.exp(-\alpha X) \quad (6)$$

$$k\frac{eff}{t} = k_t.exp(-\beta X) \quad (7)$$

Here, X denotes conversion, while α, β represent the diffusion limitation coefficients.

$$\frac{d[TDMA_1]}{d[St_2]} = \frac{[TDMA_1]\cdot\left\{\frac{[TDMA_1]}{r_{21}\cdot r_{31}} + \frac{[St_2]}{r_{21}\cdot r_{32}} + \frac{[MA_3]}{r_{23}\cdot r_{31}}\right\}}{[St_2]\cdot\left\{\frac{[TDMA_1]}{r_{21}\cdot r_{31}} + \frac{[St_2]}{r_{21}\cdot r_{32}} + \frac{[MA_3]}{r_{23}\cdot r_{31}}\right\}} \cdot \frac{\left\{[TDMA_1] + \frac{[St_2]}{r_{12}} + \frac{[MA_3]}{r_{13}}\right\}}{\left\{\frac{[TDMA_1]}{r_{21}} + [St_2] + \frac{[MA_3]}{r_{13}}\right\}} \quad (8)$$

$$\frac{d[TDMA_1]}{d[St]} = \frac{[TDMA_1]\cdot\left\{\frac{[TDMA_1]}{r_{21}\cdot r_{31}} + \frac{[St_2]}{r_{21}\cdot r_{32}} + \frac{[MA_3]}{r_{23}\cdot r_{31}}\right\}}{[MA_3]\cdot\left\{\frac{[TDMA_1]}{r_{13}\cdot r_{31}} + \frac{[St_2]}{r_{12}\cdot r_{23}} + \frac{[MA_3]}{r_{13}\cdot r_{32}}\right\}} \cdot \frac{\left\{[TDMA_1] + \frac{[St_2]}{r_{12}} + \frac{[MA_3]}{r_{13}}\right\}}{\left\{\frac{[TDMA_1]}{r_{31}} + \frac{[St_2]}{r_{32}} + [MA_3]\right\}} \quad (9)$$

ISSN 3030-3907

$$\frac{d[St_2]}{d[MA_3]} = \frac{[St_2]\cdot\left\{\frac{[TDMA_1]}{r_{21}\cdot r_{31}} + \frac{[St_2]}{r_{21}\cdot r_{32}} + \frac{[MA_3]}{r_{23}\cdot r_{32}}\right\}}{[MA_3]\cdot\left\{\frac{[TDMA_1]}{r_{13}\cdot r_{31}} + \frac{[St_2]}{r_{12}\cdot r_{23}} + \frac{[MA_3]}{r_{13}\cdot r_{23}}\right\}} \cdot \frac{\left\{\frac{[TDMA_1]}{r_{21}} + [St_2] + \frac{[MA_3]}{r_{23}}\right\}}{\left\{\frac{[TDMA_1]}{r_{31}} + \frac{[St_2]}{r_{32}} + [MA_3]\right\}} \quad (10)$$

Here, r_{ij} / r_{ji} are the reactivity ratios (terpolymerization reaction parameters) for the *i/j* monomer pair, and $[M_i]$ denotes the monomer concentration.

Determination of reactivity ratios: For a ternary system, the reactivity ratios are determined based on the extended form of copolymerization equations. The general form of the Alfred Goldfinger equation for evaluating reactivity coefficients is expressed as follows:

$$\frac{d[TDMA_1]}{d[St_2]} = \frac{[TDMA_1]\cdot\left\{\rho\cdot\frac{[TDMA_1]}{r_{21}} + \frac{[St_2]}{r_{21}} + \rho\cdot\frac{[MA_3]}{r_{23}}\right\}}{[St_2]\cdot\left\{\rho\cdot\frac{[TDMA_1]}{r_{12}} + \frac{[St_2]}{r_{12}} + \frac{[MA_3]}{r_{13}}\right\}} \cdot \frac{\left\{[TDMA_1] + \frac{[St_2]}{r_{12}} + \frac{[MA_3]}{r_{13}}\right\}}{\left\{\frac{[TDMA_1]}{r_{21}} + [St_2] + \frac{[MA_3]}{r_{13}}\right\}} \quad (11)$$

$$\frac{d[TDMA_1]}{d[MA_3]} = \frac{[TDMA_1]\cdot\left\{\rho\cdot\frac{[TDMA_1]}{r_{21}} + \frac{[St_2]}{r_{21}} + \rho\cdot\frac{[MA_3]}{r_{23}}\right\}}{[MA_3]\cdot\left\{\rho\cdot\frac{[TDMA_1]}{r_{13}\cdot r_{21}} + \frac{[St_2]}{r_{12}\cdot r_{23}} + \frac{[MA_3]}{r_{13}\cdot r_{23}}\right\}} \cdot \frac{\left\{[TDMA_1] + \frac{[St_2]}{r_{12}} + \frac{[MA_3]}{r_{13}}\right\}}{\{\rho\cdot[TDMA_1] + [St_2]\}} \quad (12)$$

$$\frac{d[St_2]}{d[MA_3]} = \frac{[St_2]\cdot\left\{\rho\cdot\frac{[TDMA_1]}{r_{12}} + \frac{[St_2]}{r_{12}} + \frac{[MA_3]}{r_{13}}\right\}}{[MA_3]\cdot\left\{\frac{[TDMA_1]}{r_{13}\cdot r_{21}} + \frac{[St_2]}{r_{12}\cdot r_{23}} + \frac{[MA_3]}{r_{13}\cdot r_{23}}\right\}} \cdot \frac{\left\{\frac{[TDMA_1]}{r_{21}} + [St_2] + \frac{[MA_3]}{r_{23}}\right\}}{\{\rho\cdot[TDMA_1] + [St_2]\}} \quad (13)$$

$$\rho = \frac{k_{31}}{k_{32}} \quad (14)$$

Here, [Mi] denotes the monomer concentration, r_{ij}/r_{ji} represent the terpolymerization parameters (reactivity ratios) of the monomers, where M1 - TDMA, M2 - ST, M3 - MA.

ISSN 3030-3907

Mathematical modeling: The terpolymerization process was described using a mathematical model. The model is based on the following system of differential equations:

$$\frac{d[M_i]}{dt} = -k_p[M_i][R^{\cdot}] \quad (14)$$

$$\frac{d[R^{\cdot}]}{dt} = 2fk_d[I] - k_t[R^{\cdot}]^2 \quad (15)$$

The model parameters were adjusted as a function of conversion while accounting for diffusion limitations. The optimal kinetic conditions were determined based on the Fisher diagram, and maximum efficiency was observed under the following condition:

$$k_t/k_p \rightarrow max \quad (17)$$

Under these conditions, terpolymers with high molecular weight and narrow polydispersity are formed.

Effect of initiator (IMDN) concentration on terpolymerization kinetics: In the terpolymerization process involving TDMA, styrene, and maleic anhydride, the effects of reaction time, initiator type and concentration, solvent nature, and temperature variation on monomer conversion, as well as on the molecular weight and structural formation of the resulting terpolymer, were investigated.

Table 2

Effect of IMDN concentration on the terpolymerization rate at 95 ± 5 °C for 150 minutes

Sample №	IMDN × 10^{-6} mol·L^{-1}	Conversion, %	R_p × 10^{-6} mol·L^{-1}·s^{-1}
1	16.8	6.4	4.075
2	25.2	8.2	4.89
3	33.6	10.6	5.705
4	42.0	12.4	7.335
5	51.3	15.2	8.965

[TMDA]=2.01 mol. L^{-1}, [St] = 1.44 mol. L^{-1}, [MA] 0.72 mol. L^{-1}

ISSN 3030-3907

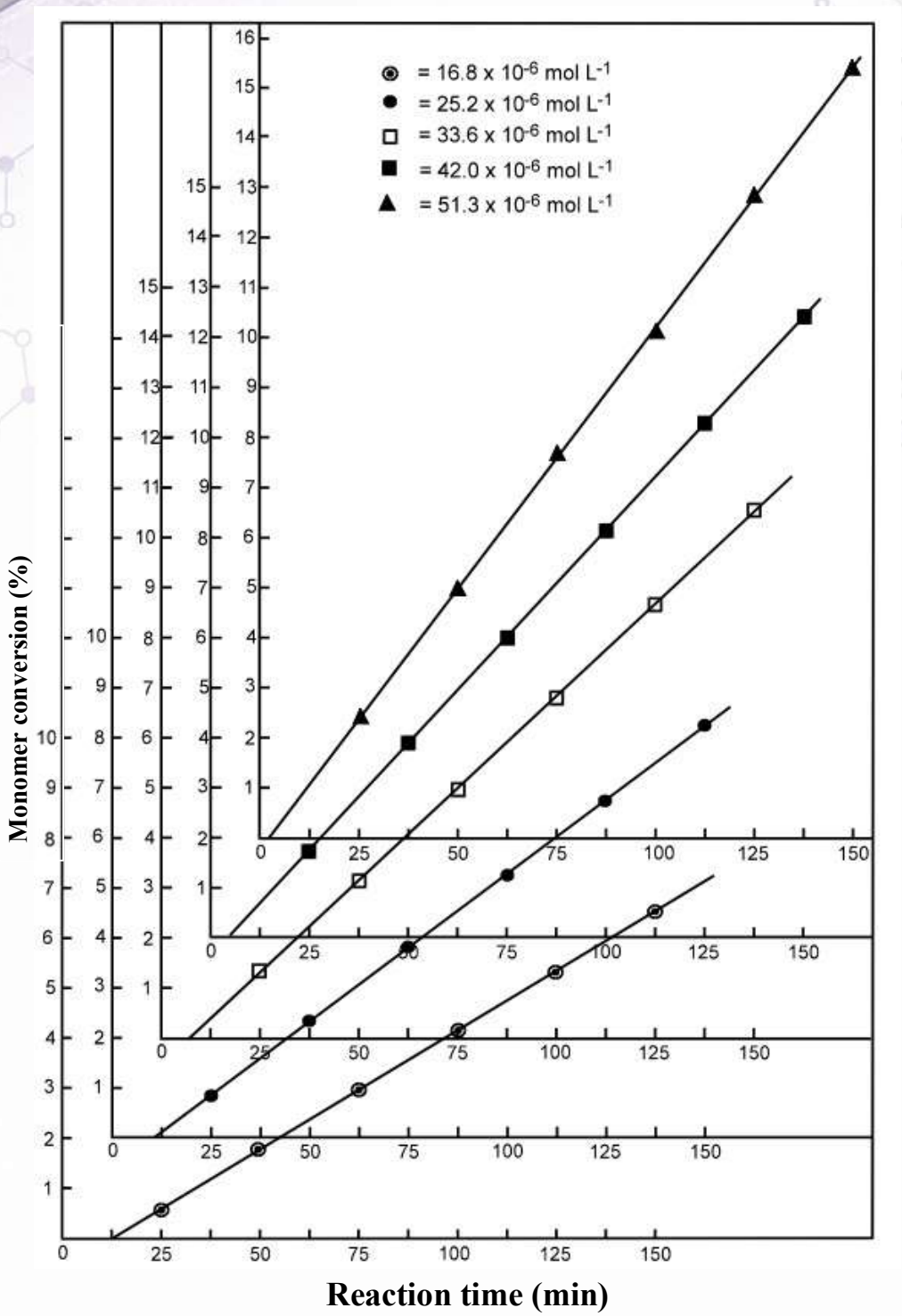


Figure 1. Effect of time on the conversion of TDMA, styrene (St), and maleic anhydride (MA) in terpolymerization at 95–105 °C in the presence of the initiator (IMDN)

These results indicate that with increasing concentration of the IMDN initiator, the number of active radicals increases, leading to an acceleration of chain propagation reactions. This behavior is consistent with the fundamental equation of radical polymerization kinetics (Eq. 3), according to which the polymerization rate is proportional to the square root of the initiator concentration. At low initiator concentrations (16.8×10^{-6} mol·L^{-1}), the limited number of active centers results in

ISSN 3030-3907

a slower incorporation of monomers into the polymer chain. As the concentration increases, the number of active centers rises, enhancing the incorporation rate of TDMA, styrene, and maleic anhydride into the growing chain. The results also demonstrate that within the temperature range of 95–105 °C, the initial stages of the process proceed under kinetic control, and diffusion limitations are not yet significant.

Furthermore, the nearly linear increase in conversion and reaction rate confirms that the system follows pseudo-first-order kinetics (Eq. 5). The results indicate that the terpolymerization process in the TDMA–St–MA system can be effectively controlled by adjusting the initiator concentration. This provides a practical opportunity to tailor the structure and properties of functional terpolymers. In addition, the obtained results serve as a basis for determining reactivity ratios and optimizing the parameters of the kinetic model in subsequent stages.

Initial incorporation behavior of monomers at low conversion: The experimental results obtained for TDMA–St–MA terpolymers synthesized at different monomer ratios in the low conversion region ($X_v \approx 0.02–0.09$) were used to evaluate the initial incorporation behavior of the monomers. The results for three optimal initial composition combinations are presented in Table 3.

Table 3

Experimental data for TDMA–St–MA terpolymerization at low conversion (temperature 95 ± 5 °C, IMDN, reaction time 150 ± 5 min)

Optimal initial composition (mol ratio)	X_w (conversion)	f TDMA,0	f St,0	f MA,0	F TDMA	F St	F MA,0
1	0.066	0.8	0.1	0.1	0.761	0.135	0.104
	0.071	0.8	0.1	0.1	0.778	0.137	0.085
	0.083	0.8	0.1	0.1	0.783	0.136	0.081
	0.091	0.8	0.1	0.1	0.750	0.146	0.104
2	0.036	0.1	0.8	0.1	0.123	0.826	0.052
	0.043	0.1	0.8	0.1	0.122	0.824	0.054
	0.071	0.1	0.8	0.1	0.107	0.836	0.057
	0.079	0.1	0.8	0.1	0.115	0.817	0.069
	0.088	0.1	0.8	0.1	0.110	0.823	0.067
3	0.021	0.1	0.2	0.7	0.123	0.374	0.503
	0.025	0.1	0.2	0.7	0.121	0.382	0.496

ISSN 3030-3907

	0.030	0.1	0.2	0.7	0.122	0.384	0.494
	0.034	0.1	0.2	0.7	0.118	0.368	0.514
	0.040	0.1	0.2	0.7	0.117	0.372	0.511
	0.056	0.1	0.2	0.7	0.125	0.377	0.498
	0.059	0.1	0.2	0.7	0.124	0.374	0.502
	0.064	0.1	0.2	0.7	0.121	0.368	0.511
	0.087	0.1	0.2	0.7	0.114	0.344	0.542

X_w – *conversion,*

$f_i,0$ – *initial monomer composition (i-th monomer),*

F_i – *cumulative terpolymer composition.*

According to the results presented in Table 3, for the system with the initial composition (TDMA = 0.8; St = 0.1; MA = 0.1), the conversion varies within the range of 0.066–0.091. The terpolymer composition shows that the TDMA fraction is F_{TDMA}=0,750–0,783, the styrene fraction is F_{St}=0,135–0,146, while the maleic anhydride fraction remains comparatively low. The high content of TDMA in this system indicates its stable incorporation into the growing polymer chain and its kinetic predominance, which can be attributed to the active participation of long-chain alkyl methacrylates in radical propagation.

For the system with the initial composition (TDMA = 0.1; St = 0.8; MA = 0.1), the conversion varies within the range of 0.036–0.088. The terpolymer composition is dominated by styrene, with F_{St}=0,817–0,836, while the TDMA fraction is lower and the maleic anhydride fraction is F_{MA}=0,052–0,069. The high incorporation of styrene is attributed to its high reactivity in radical processes and its donor characteristics. Furthermore, the donor–acceptor interaction between styrene and maleic anhydride enhances its active participation in copolymerization.

For the system with the initial composition (TDMA = 0.1; St = 0.2; MA = 0.7), the conversion ranges from 0.021 to 0.087. The terpolymer composition reveals that the maleic anhydride fraction is F_{MA}=0,494–0,542,, the styrene fraction is F_{St}=0,344–0,384, and the TDMA fraction is F_{TDMA}=0,114–0,125. Despite its low tendency toward homopolymerization, the relatively high incorporation of maleic anhydride indicates that, within the ternary system, it forms a complex with styrene and is actively incorporated into the growing polymer chain.

These results indicate that, in the low conversion region, the terpolymer composition remains close to the initial monomer composition; however, certain deviations are observed due to differences in monomer reactivity. In general, the composition changes in accordance with the overall terpolymerization kinetic equations for ternary systems (Eqs. 8–10). The results also demonstrate that under low conversion conditions, the relationship $F_i \approx f_i$ is maintained, although slight

ISSN 3030-3907

deviations confirm the presence of reactivity ratios in ternary terpolymerization systems. This highlights the necessity of considering ternary reactivity coefficients when developing a kinetic model for the TDMA–St–MA system. Furthermore, the systematic deviation of Fi from f_i indicates that each monomer plays an individual kinetic role in the formation of the terpolymer microstructure. Therefore, these findings provide an important experimental basis for determining reactivity ratios and for the mathematical modeling of the terpolymerization process.

Dependence of terpolymer composition on conversion and comparison with the kinetic model: The degree of monomer incorporation into the polymer chain during the terpolymerization of the synthesized monomer mixtures was evaluated using the cumulative composition function *Fi*. The experimental results were compared with the values predicted by the kinetic model (Figure 2).

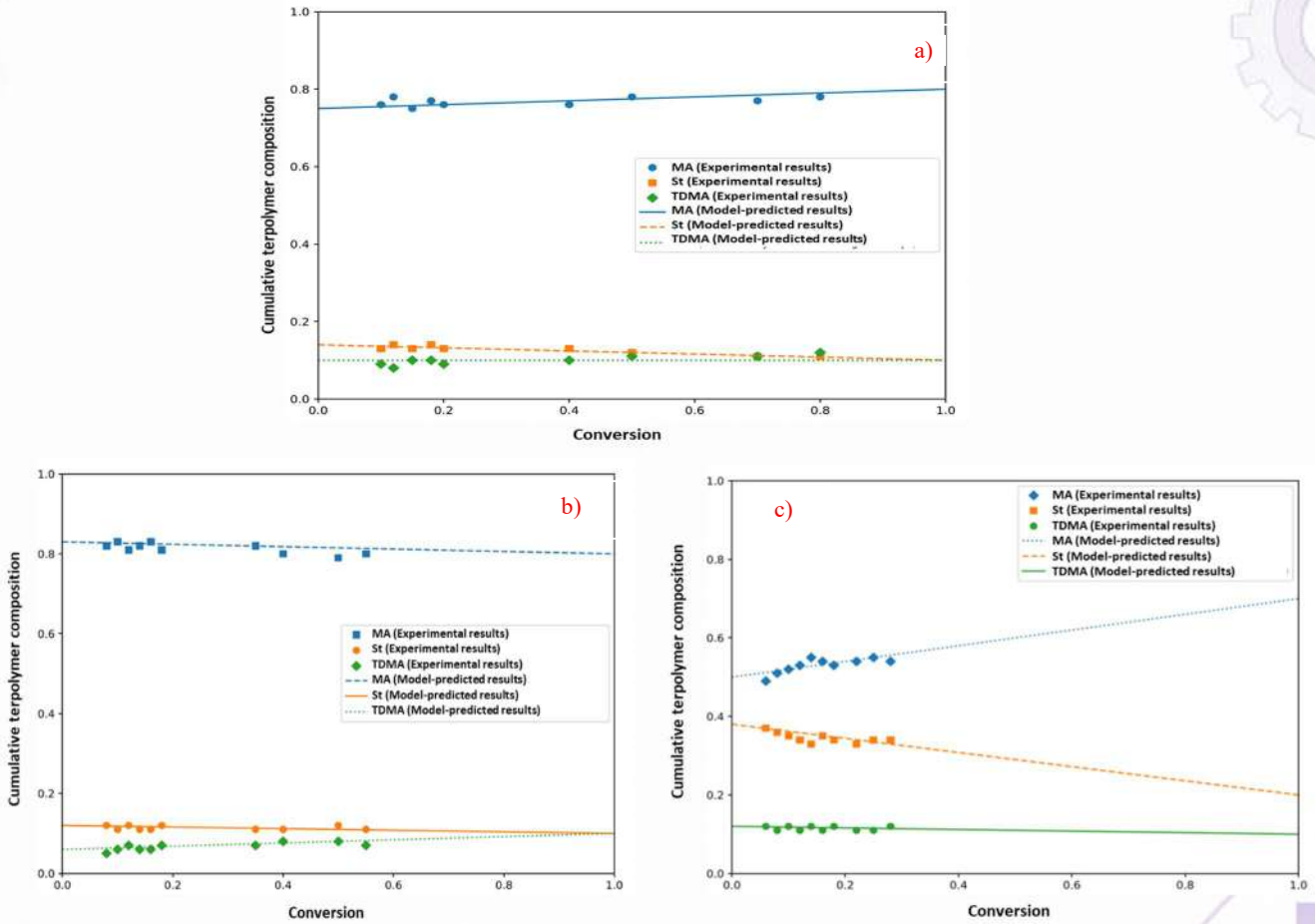


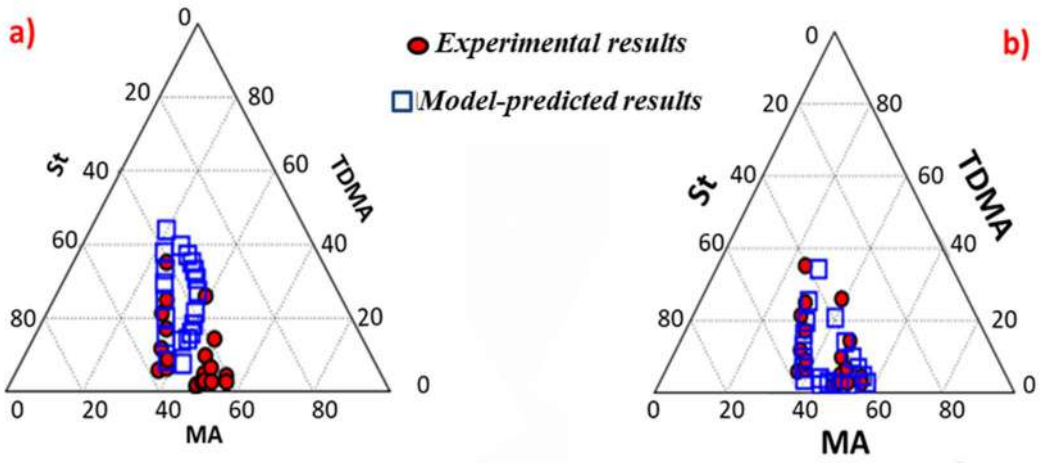
Figure 2. Cumulative terpolymer composition *Fi* for TDMA–St–MA monomer ratios: (a) 0.8/0.1/0.1, (b) 0.1/0.8/0.1, and (c) 0.1/0.2/0.7 (experimental data and model predictions)

For the initial composition (0.8/0.1/0.1), when the conversion varies within the range of 0.05–0.90, the TDMA fraction as the main component in the terpolymer remains nearly constant at F≈0,75–0,80, while the fractions of the second and third monomers are approximately F≈0,12–0,15, with only minor variations (±0.02) as conversion increases. Similarly, for the (0.1/0.8/0.1) system,

ISSN 3030-3907

styrene remains the dominant component throughout the entire conversion range, with a fraction F≈0,80–0,83, while TDMA and MA fractions are ≈0,10–0,13 and F≈0,06–0,10, respectively. In contrast, for the (0.1/0.2/0.7) system, a noticeable compositional redistribution is observed with increasing conversion. At low conversion, the MA fraction is F≈0,50–0,55, whereas at high conversion it increases to F≈0,65–0,70. At the same time, the styrene fraction decreases to F≈0,35–0,40, while the TDMA fraction remains relatively stable at F≈0,10–0,12. For all ternary systems studied, the values calculated using the kinetic model show a high degree of agreement with the experimental results, with a maximum deviation not exceeding ±0.02–0.04. The overall agreement (within ±0.03 accuracy) confirms the validity of the selected mathematical approach and the adequacy of the kinetic model. The model enables reliable prediction of terpolymer composition evolution and demonstrates that, by adjusting the TDMA–St–MA monomer ratios, it is possible to tailor the final structure and properties of the terpolymers. Furthermore, the obtained results provide a robust experimental basis for determining reactivity ratios.

Determination of reactivity ratios and adequacy of the kinetic model: Figure 3 presents the experimental data points of terpolymer composition in the TDMA–St–MA system along with the values calculated using the kinetic model, shown in a ternary diagram. In accordance with kinetic equations (11–13), Figure 3(a) illustrates the model results calculated based on binary reactivity ratios, while Figure 3(b) shows the model predictions obtained using ternary reactivity ratios, both compared with the experimental data.



3-Figure. Experimental and calculated (model-based) terpolymer composition for the TDMA/St/MA system: (a) binary reactivity coefficients, (b) ternary reactivity coefficients

According to the results shown in Figure 3(a), the values calculated based on the binary model exhibit significant deviations from the experimental data points,

ISSN 3030-3907

indicating that the binary approach is insufficient to fully describe the terpolymer composition in ternary systems. In contrast, the results presented in Figure 3(b) demonstrate that the model based on ternary reactivity ratios shows a much closer agreement with the experimental data. The maximum deviation between the model predictions and experimental results does not exceed ±0.03, confirming the improved accuracy of the ternary approach. These findings indicate that the mutual reactivity of monomers in the TDMA–St–MA system cannot be fully described solely by pairwise interactions, and the presence of a third monomer significantly affects the kinetic parameters. Thus, the comparison of experimental and calculated terpolymer compositions in the TDMA–St–MA system demonstrates that the ternary reactivity ratio model (based on Eq. 14) provides a more accurate representation of the system than the binary model.

TDMA-St-MA

$$r_{12}\frac{k_{TDMA}}{k_{St}}=\frac{k_{p1}}{k_{p12}}=\frac{k_{f1}}{k_{Sf12}}=0{,}994; \qquad r_{21}\frac{k_{St}}{k_{TDMA}}=\frac{k_{p2}}{k_{p21}}=\frac{k_{f2}}{k_{Sf21}}=1{,}621$$

$$r_{13}\frac{k_{TDMA}}{k_{MA}}=\frac{k_{p1}}{k_{p13}}=\frac{k_{f1}}{k_{Sf13}}=2{,}022; \qquad r_{31}\frac{k_{MA}}{k_{TDMA}}=\frac{k_{p2}}{k_{p31}}=\frac{k_{f2}}{k_{f31}}=0{,}343$$

$$r_{12}\frac{k_{MA}}{k_{St}}=\frac{k_{p1}}{k_{p32}}=\frac{k_{f1}}{k_{Sf32}}=0{,}994; \qquad r_{23}\frac{k_{St}}{k_{MA}}=\frac{k_{p2}}{k_{p31}}=\frac{k_{f2}}{k_{Sf31}}=0{,}315$$

The obtained results indicate that for the TDMA–styrene pair, the reactivity ratios were determined as $r_{12}\approx0.99$, suggesting nearly statistical copolymerization, while the chain end terminated with styrene exhibits higher reactivity toward TDMA. For the TDMA–MA pair, the values r_{13}va $r_{31}\approx0.34$ were obtained, indicating that a TDMA-ended chain has a high tendency to react with MA monomer, whereas an MA-ended chain shows lower reactivity toward TDMA. Similarly, for the styrene–MA pair, the reactivity ratios $r_{23}\approx$ indicate that a styrene-ended chain has a higher probability of reacting with MA, while an MA-ended chain exhibits lower reactivity toward styrene.

Based on these findings, the terpolymerization reaction can be described as follows:

ISSN 3030-3907

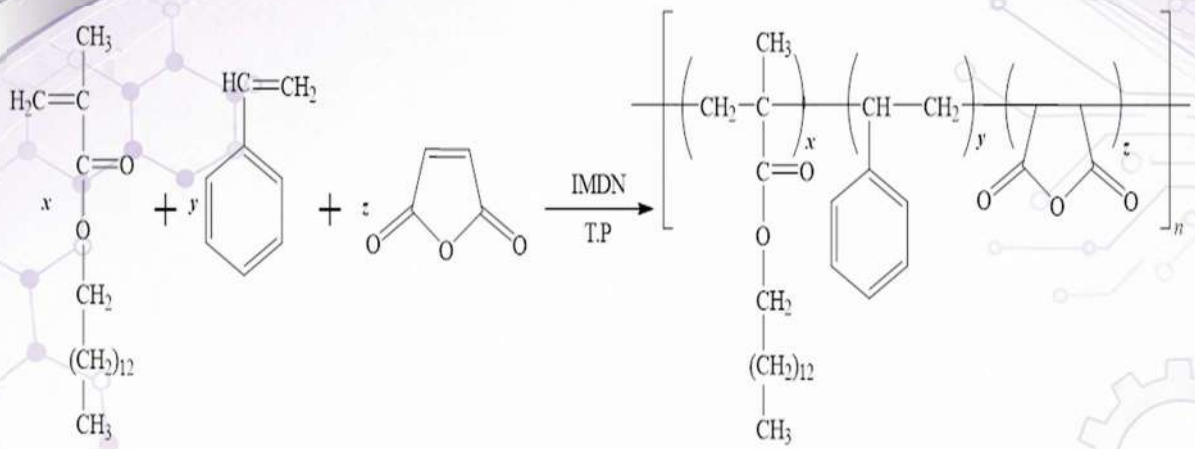


Figure 4. Terpolymerization reaction scheme

The mutual reactivity of TDMA–St–MA monomers is governed by a complex ternary kinetic mechanism. For the TDMA–styrene pair, the value $r_{12}=1$ indicates a nearly statistical distribution of monomers during chain growth, while $r_{21}>1$ reflects a higher tendency of styrene to be incorporated compared to TDMA, leading to an alternating arrangement of elastic (TDMA) and rigid (styrene) segments within the polymer chain. For the TDMA–MA pair, the observed ratios $r_{13}\gg1$ and $r_{31}\ll1$ indicate that maleic anhydride has a low tendency for homopolymerization; however, in the presence of TDMA, it is effectively incorporated into the terpolymer chain. This suggests that MA is incorporated primarily through reactions with other monomers and acts as a functional fragment within the polymer structure. For the styrene–MA pair, the values $r_{23}>1$ and $r_{32}<1$confirm the presence of a donor–acceptor mechanism, where styrene acts as a donor and maleic anhydride as an acceptor, resulting in the formation of partially alternating segments in the polymer chain.

The deviation of the binary model from the experimental results indicates that the presence of a third monomer in ternary systems significantly alters the kinetic constants. Therefore, a model that accounts for ternary reactivity ratios is required for an accurate description of the terpolymerization process. The high agreement of the ternary model with the experimental data (within ±0.03 accuracy) confirms its adequacy and demonstrates its capability to reliably predict terpolymer composition. Moreover, this approach enables simultaneous control of key material properties such as elasticity, viscosity, and functional performance of the resulting terpolymers.

CONCLUSION

The kinetic regularities of the terpolymerization process in the TDMA–styrene–maleic anhydride (TDMA–St–MA) system were comprehensively investigated, the monomer reactivity ratios were determined, and the adequacy of the developed kinetic model was validated against experimental data. It was

ISSN 3030-3907

established that an increase in the initiator (IMDN) concentration leads to a nearly linear increase in both the terpolymerization rate and monomer conversion. The initial stages of the process follow pseudo-first-order kinetics, highlighting the decisive role of active radical concentration in radical terpolymerization. The results obtained in the low conversion region (X_w = 0,02–0,09) indicate that the initial incorporation of monomers is close to the feed composition; however, slight deviations occur due to differences in reactivity ratios. TDMA and styrene exhibit higher reactivity and predominantly determine the terpolymer composition, whereas maleic anhydride, despite its low tendency for homopolymerization, is selectively incorporated into the polymer chain through a donor–acceptor mechanism.

Overall, the terpolymers formed in the TDMA–St–MA ternary system consist of statistically distributed and partially alternating segments, where TDMA contributes to elastic properties, styrene provides mechanical strength, and maleic anhydride introduces functional groups. Furthermore, controlling the terpolymerization process enables the design of functional terpolymer additives with targeted physicochemical properties. These findings provide a scientific basis for the synthesis of highly efficient terpolymer additives for fuel and lubricant applications.

REFERENCES

1. James G. Speight The Chemistry and Technology of Petroleum, 5th ed., CRC Press, Boca Raton, 2014, pp. 811–835.
2. Fuel and Lubricant Additives Chemistry and Applications Totten Westbrook Shah, 2nd ed., CRC Press, Boca Raton, 2003, pp. 3–28.
3. Danilov A.M. The current state of production and use of additives in the production of diesel fuel Euro-3, 4, 5: Report on the joint session of the VNIINP and Committee on fuel and issues ANN RF / A.M. Danilov. - M.: Izd-vo "Sputnik+", 2009. - 27 p.
4. Vincent, M., Richards, W., Cook, P.J., Leonard, S. (2002). Fuel additives. US Patent 6,488,725, December 3.
5. Ribeaud M., Dubs P., Rasberger M., Evans, S. (2001). Liquid polyfunctional additives for improved fuel lubricity. US Patent 6,296,677, October 2.
6. D. T. Gentekos, R. J. Sifri and B. P. Fors, Controlling Polymer Properties through the Shape of the Molecular-Weight Distribution, Nat. Rev. Mater., 2019, 4(12), 761–774, DOI: 10.1038/s41578-019-0138-8.
7. Mavlonov Shokhrukh Synthesis of copolymers based on dodecyl metacrylate and styrene and investigation of their effect on low-temperature and physico-chemical properties of diesel fuel // Universum: технические науки: электрон.

научн. журн. 2023. 3(108). URL: https://7universum.com/ru/tech/archive/item/15164
8. Leslie R. Rudnick Lubricant Additives Chemistry and Applications, 3rd ed., CRC Press, Boca Raton, 2017, pp. 245–278.
9. George E. Totten Fuels and Lubricants Handbook, ASTM International, West Conshohocken, 2003, pp. 421–450.
10. George Odian Principles of Polymerization, 4th ed., John Wiley & Sons, New York, 2004, pp. 425–470.
11. Mayo Lewis copolymerization equation original concept Fineman Ross method polymer kinetics Fineman, M., Ross, S. D., "Linear method for determining monomer reactivity ratios in copolymerization," *Journal of Polymer Science*, 1950, Vol. 5, pp. 259–262.
12. Encyclopedia of Polymer Science and Technology styrene maleic anhydride copolymer, Wiley, New York, 2003, Vol. 11, pp. 1–25.
13. George Odian Principles of Polymerization styrene maleic anhydride alternating copolymer, 4th ed., John Wiley & Sons, 2004, pp. 460–468.
14. PREDICI polymer reaction engineering software polymer kinetics modeling Wulkow Wulkow, M., *PREDICI® – Simulation of Polymer Reaction Engineering*, Wiley-VCH, Weinheim, 2008, pp. 55–102.
15. Monte Carlo simulation polymerization kinetics modeling polymer science Frenkel, D., Smit, B., *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed., Academic Press, 2002, pp. 487–520.
16. Mavlonov Shohrux Boboxon o`g`li, Fozilov Sadriddin Fayzullayevich**.** **U**ch monomerli terpolimerlanishda radikal rekombinatsiya va disproportsiyalanish jarayonlarini tahlil qilish // Ilmiy – texnikaviy xalqaro konferensiya BUXORO – 2026, 10 aprel. 412-415 b.
17. Mavlonov Shohrux Boboxon o`g`li, Fozilov Sadriddin Fayzullayevich**.** Alfred goldfinger kinetik tenglamasi asosida terpolimerlanish jarayonining matematik modellashtirilishi (TDMA, ST,MA misolida) // Ilmiy – texnikaviy xalqaro konferensiya BUXORO – 2026, 10 aprel. 416-419 b.