Turkish Online Journal of Qualitative Inquiry (TOJQI)
Volume 12, Issue6, July , 7451- 7460

Research Article

Study Of Copolymers Synthesized By The Compensation Method As Modifiers Of Viscosity-Lubricant Oils

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Abstract:

The Increasing Requirements For Polymer Materials Pose The Task Of Obtaining High-Molecular Compounds With New Properties As One Of The Most Important. There Are Different Approaches To Solving This Problem, And Modification In The Process Of Synthesis Of Polymer Molecules Is A Separate Group Of Studies. The Main Task In This Case Is To Change The Conditions At The Synthesis Stage, Which Would Lead To New Properties, While Preserving The Complex Of Valuable Properties Of The Polymer As Much As Possible.

Keywords: Copolymers, Terpolymers, Ir Spectroscopy

New Copolymers Synthesized In The Presence Of Various Initiators And With A Commensurate Ratio Of Components Using The Compensation Method Have Low Mm Values And A Compositionally Homogeneous Structure. This Suggested That How

Introduction

And Similar Copolymers Ama With Vae, They Can Have Good Thickening Properties In Mineral And Synthetic Base Oils. In This Case, The Homogeneity Of Their Structure Will Manifest Itself In Resistance To Destruction. To Implement This Assumption, A Preliminary Assessment Of The Solubility Of Copolymers (Vbe-Ba, Ba-St, Ega-St And Bma-St, Vbe-Ba-St, Vbe-Ega-St And Vbe-Bma-St) In Petroleum And Synthetic Bases Of Oils Was Carried Out. The Solubility Of Copolymers In Oils Was Determined By Studying The Dissolution Of Copolymers At A Concentration Of 5 Wt% In The Mineral Base Of Amg-10 Oil And The Synthetic Base Of Dos Upon Heating And Stirring, Followed By Cooling To Room Temperature. The Results Are Shown In Table. 12. As Can Be Seen From The Data Table. 12, Synthesized Samples Of Copolymers (Vbe-Ba, Vbe-Ega-St, Vbe-Ba-St) Are Of Practical Interest As Thickeners, Since Dissolve In Dos And Amg-10 With The Formation Of Stable Solutions At 250c. It Can Be Seen That All Copolymers Are Readily Soluble In Dos, And In Amg-10, The Vbe-Ba Copolymers Obtained On All Types Of Initiators, As Well As Ternary Copolymers Vbe-Ega-St And Vbe-Ba-St, Obtained By Sequential Dosing Of Active Monomers. Unlike The Vbe-Ba-St Copolymer (Sequential Dosing), The Vbe-Ba-St Copolymer (Joint Dosing) Did Not Dissolve In The Mineral Base. Based On The Data On The Composition Of The Copolymers, It Can Be Assumed That The Vbe Content Is Close To 50 Mol. % Ensures The Solubility Of The Copolymer In The Amg-10 Oil Base.

Table 1.

Solubility Of The Synthesized Copolymers In The Mineral Base Of Amg-10 Oil And The Synthetic Base Of Dos.

A Type Copolymer	Initiator	$M_n\times10^{-3}$	Solubility In Dos At 25^0c	Solubility In Amg-10 At 25^0c
Ba-Vbe	Dak	15-20	+	+
	Teb+O_2	13	+	+
	Tnb +O_2	18	+	+
	Tnb + Dps	28	+	+
Ba-St	Дак	9,1-21,1	+	-
Ega-St		21,2	+	-
Bma-St		18,1	+	-
Vbe-Ba-St		9,7	+	-**
Vbe-Ba-St *		6,3	+	+
Vbe-Ega-St		10,9	+	+
Vbe-Ega-St		9,3	+	-**

* Sequential Dosing Of Ba For 30 Min, Then St For 30 Min, Dak Is Evenly Distributed In The Monomers To Be Dosed, The Composition Of The Copolymer Vbe-Ba-St (43-45) :(38-40) :(16-18) Mol. % By Ir.

** When Heated To 100^0c They Dissolve, And When The Solution Is Cooled, The Copolymer Precipitates Again.

Data On The Thickening Effect Of Solutions In Dos Of Copolymers Of Ba With Vbe At Positive Temperatures, Synthesized In The Presence Of Organoelement Initiators In Comparison With Aibn. It Can Be Seen That A Slightly Higher Kinematic Viscosity Is Observed In The Case Of Using Systems With Tab In The Preparation Of Copolymers, Which May Be Associated With The Peculiarities Of The Formation Of Macromolecular Chains In Their Presence. Tests Of Ba-Vbe Copolymers Obtained Using Tab As Initiators As Mw Dos Did Not Reveal Any Noticeable Difference In Terms Of The “Degree Of Destruction” (D,%) Parameter From Those Synthesized In The Presence Of Aibn. In This Regard, The Use Of Boron-Containing Initiators, Which Are Rather Expensive, Is Not Promising For The Preparation Of Copolymers And Was Not Carried Out In Further Work.

Comparison Of Ba-Vbe Copolymers As A Thickener With Domestic And Imported Additives Of A Similar Effect For A Number Of Characteristics Indicates A Comparable Effect In Dos. In Terms Of “Degree Of Destruction” (D,%), The New Ba-Vbe Copolymers In Dos Solution Are Superior To Domestic Acrylate Additives Pma V-1 And Pma V-2, As Well As The Imported Viscoplex 7-302 Thickener. A Small Variation In The Low-Temperature Viscosity Of The Copolymer Solution During Its Preparation In The Presence Of Aibn By Introducing The Active Monomer

Uniformly Or In Portions. Also, The Values Of Kinematic Viscosity Are Comparable At Positive Temperatures And Noticeably Less At Temperatures Of -40^{0}c. This Is Most Likely Due To The Presence Of A Noticeably Larger Low Molecular Weight Fraction In The Copolymer During Batch Dosing When Compared With That Obtained By Uniform Dosing. This, In Turn, Leads To A Larger Value Of The Polydispersity Coefficient Of The Samples.

Table 2.

Characteristics Of 5% Thickener Solutions In Dos.

№	Conditions For The Synthesis Of Ba-Vbe Copolymers (Initiator And Its Concentration) / Analogs	Kinematic Viscosity At A Temperature, ^{O}c			Viscosity Index	D,%
		40	100	-40		
1	Without Additives	-	3,20	-	-	-
2	Dak (0,4 Mol.%)	-	4,35		211	5-7
3	Dak**** (0,03 Mol.%)	-	4,41		-	≤10
4		18,00	6,54*	4100	218	
5			12,28**	(16-17)× 10^3**		
6	Дак (0,03 Мол. %)***		12,26**	(13-14)× 10^3**	-	
7	Teb +O_2 (0,16 Mol %)	18,60	4,92	-	209	
8	Tnb+O_2 (0,32 Mol %)	-	-	-	-	
9	Tnb + Dps (0.32 And 0.08 Mol%, Respectively)	21,10	5,48	-	222	
10	Viscoplex 0-101*	19,92	5,69	2800	258	2
11	Viscoplex 7-302*	25,31	7,38	3200	285	23
12	Pma V-1*	-	5,71	-	212	60
13	Pma V-2*	-	12,41	-	219	80

* Concentration Of Thickener 10%,

** Concentration Of Thickener 15%

*** Batch Dosing Of Ba With Dak

**** [164].

Copolymers Ama With St Are Readily Soluble In Dos, In Contrast To Insoluble Copolymers Of Vbe With St And In Comparison With Imported Analogous To Close Mm Showed A Similar Thickening Ability And High Resistance To Mechanical Destruction.

Table 3.

Characteristics Of Solutions Of Copolymers Ama-St (5 Wt.%) And Their Analogues.

№	Copolymer	Solution Viscosity In Dos At 100 ^{0}c, Mm^2 /S	D, %
1	-	3,2	-
2	Ba-St	4,7	2,6
3	Вма-St	5,0	7,9
4	Ega-St	4,1	1,0
5	Viscoplex 12-310	4,7	6,8

Table 4.

Characteristics Of Solutions Of Terpolymers (5 Wt%) And Their Analogues.

№	Additive / Terpolymer	The Viscosity Of The Solution In Dos At 100 ^{0}c, Mm^2/S	Dos, D, %	The Viscosity Of The Solution In Amg-10 At 50 ^{0}c, Mm^2/S	Amg-10 D, %
1	Pma V-2*	12,4	61	-	-
2	Viscoplex 12-310	4,7	6,8	-	-
3	Vinipol Wb -2**	-	-	10,4	41
4	Vbe-Ega-St	4,3	3,7	4,5	1,3
5	Vbe-Bma-St	4,7	5,8	N / A	N/A
6	Vbe-Ba-St	4,4	2,5	N / A	N/A
7	Vbe-Ba-St***	4,3	2,8	3,2	2,2

* The Concentration Of The Additive In The Oil Is 7 Wt. % Four

** The Concentration Of The Additive In The Oil Is 10 Wt. % Four

*** Sequential Dosing Of Ba For 30 Min, Then St For 30 Min, Daa Is Evenly Distributed In The Monomers To Be Dosed, The Composition Of The Copolymer Vbe-Ba-St (43-45) :(38-40) :(16-18) Mol. % By Ir.

Terpolymers Including Ama, St And Vbe In Dos Solution Exhibit Comparable Thickening Ability And, At The Same Time, High Resistance To Destruction In Comparison With Domestic And Imported Analogues. In Contrast To The Synthetic Base Of Dos, Not All Copolymers Exhibited Solubility In The Base Of Amg-10, Which Can Probably Be Related To The Structure Of The Copolymers. At The Base Of Amg-10, Dissolved Terpolymers Showed High Resistance To Mechanical Destruction. Thus, Studies Of New Copolymers In Oil Solutions As Thickeners Have Shown A Real Prospect Of Using Them As Resistant To Degradation Of Mb. At The Same Time, These Data Are Additional Confirmation Of The Compositional Homogeneity Of Their Structure: The Sequential Arrangement Of Monomer Units Of Different Nature In The Polymer Increases The Stability Of The Molecule. It Should Be Noted That When Obtaining Acrylate Additives To Oils To Reduce Mm, Chain Transmitters Are Introduced Into The Polymerizing Mass. In This Case, This Is Not Necessary, Which Favorably Distinguishes The Proposed Method For Producing A Copolymer As An Additive.

In The Experimental Part, We Prepared The Initial Substances, Organic Solvents: Chloroform, Toluene, Heptane, Etc., Used In The Experiments, Were Preliminarily Purified According To Generally Accepted Methods. The Physicochemical Constants Of The Solvents Used Were In Agreement With The Literature Data.

Monomers

Table 5.

Some Properties Of Vinyl Monomers

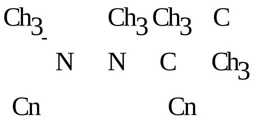
№ П/П	Monomer	Mм	Boiling T, ^{0}c/ Mmhg.	T Pl. ^{0}c	d_4^{20}	n_D^{20}	T Flashes (In A Closed Cup), ^{0}c
1	Wbe	100,16	94/760	-92	0,774	1,400	15
2	Mma	100,12	101/760 63/200 22/20	-48,2	0,943	1,4146	8
3	Ba	128,17	145/760	-64,6	0,889	-	39
4	Bma	142,20	163/760 97/90 83,5/51	-76,0	0,895	1,4220	48
6	Ega	184,28	215/760	-90	0,885	1,436	175
6	St	104,15	142,5/760	-30,6	0,909	1,5439	31
7	A-Ms	170	164/760	-23	0,896	1,543	48

Vbe Was Used Without Additional Purification. Other Monomers (Mma, Ba, Bma, Eha, St - Commercial Products) Were Preliminarily Purified From The Stabilizer (Hydroquinone) By Repeated Washing With A 10% Alkali Solution (Naoh) Until The Aqueous Phase Was Discolored, And Then Water Until Neutral, Dried Over Anhydrous Cacl2. For The Synthesis, Freshly Distilled Organic Monomers Were Taken, Which Were Purified By Vacuum Distillation. The Physicochemical Constants Of The Monomers Corresponded To The Literature Data; Some Properties Of The Used Vinyl Monomers Are Presented In Table. 5. Scc Was Synthesized According To The Method, Stored In A Glass Bottle With A Tightly Ground-In Lid In An Argon Atmosphere In A Dark Place Under Normal Conditions.

The Initiators Were: Daa, Tab (Teb And Tnb), Which Were Introduced Into The Reaction Mixture In The Form Of An Amine Complex, Which Was Destroyed By The Introduction Of Maa, In A Composition With A Co-Initiator O2, As Well As Dps.

Table 6.

Dak Characteristics

Initiator	E_{av},	Temperature, ^{O}c For □$_{1/2}$		
	Kj / Mol	0,1 H.	1 H.	10 H.
Dak  Ch_3 $Ch_3 Ch_3$ C N N C Ch_3 Cn Cn	130,23	101	82	64

Dak Is A Commercial Product, Purified By Recrystallization From Ethanol. The Physicochemical Constants Were Consistent With The Literature Data. Dak Was Stored At A Low Temperature (-(10 -15) ^{0}c).

Commercial Boramine Complexes Were Used Without Preliminary Preparation; Mac Was Purified Similarly To Monomers (Mma, Ba, Bma, Eha, St) Immediately Before The Experiment.

Dps Was Synthesized And Stored Under Normal Conditions.

Determination Of The Relative Activities Of Monomers In The Presence Of Organic Element Initiators

To Determine The Relative Activities Of Ba-Vbe Comonomers In The Presence Of Organic Element Initiators, Copolymers Were Synthesized From The Monomer Mixture In Evacuated Ampoules With Sequential Freezing Of The Introduced Reagents In Liquid Nitrogen To Prevent The Uncontrolled Course Of The Reaction. In The Experiment, We Used Monomer Mixtures With Different Component Ratios. Copolymers Were Isolated At A Conversion Of 5-7%. The Calculation Of The Relative Activities Was Carried Out Using The Kehlen-Tudos Method [254]. In This Case, For The Equation Of The Composition Of The Copolymer, A Method Of Linearization Of The Equation Of Composition Was Proposed, Taking Into Account The Degree Of Scatter Of The Experimental Data Using The Factor A.

$$[M_1] \square [M_1] R_1[M_1] \square [M_2]$$

$$[M_2] \quad [M_2][M_1] \square R_2[M_2]$$

M1 And M2 - The Content Of Monomers In The Copolymer, Mol%;

M1 And M2 - The Content Of Monomers In The Monomer Mixture, Mol%.

$$\mathrm{H} = \mathrm{R}_1\Xi - \frac{\mathrm{R}_2}{\mathrm{A}}(1 - \Xi), \quad \text{Где}$$

$$\mathrm{H} = \frac{([M_1]/[M_2])\{([m_1]/[m_2]) - 1\}}{[m_1]/[m_2]} \div \left(\alpha + \frac{([M_1]/[M_2])^2}{[m_1]/[m_2]}\right)$$

$$\Xi = \frac{([M_1]/[M_2])^2}{[m_1]/[m_2]} \div \left(\alpha + \frac{([M_1]/[M_2])^2}{[m_1]/[m_2]}\right)$$

$$\mathrm{A} = \sqrt{\left\{\frac{([\mathrm{M}_1]/[\mathrm{M}_2])^2}{[\mathrm{M}_1]/[\mathrm{M}_2]}\right\}_{\mathrm{Min}} \left\{\frac{([\mathrm{M}_1]/[\mathrm{M}_2])^2}{[\mathrm{M}_1]/[\mathrm{M}_2]}\right\}_{\mathrm{Max}}}$$

Min And Max Are Extreme Values Of The Ratios Of Quantities From A Series Of Experimental Data.

The Composition Of The Copolymers Was Determined Using The Method Of Ir Spectroscopy, The Method Is Described In The Corresponding Section. The Data Obtained As A Result Of Calculations Of □, □ And □ Are Presented In Table. 7.

Table 7.

Data For Calculating The Relative Activities Of Vbe-Ba According To The Kehlen-Tudosh Method.

[M2]	[M1]	[M2]	[M1]	[M1]/[M2]	[M1]/[M2]	A	Ξ	Η
1	2	3	4	5	6	7	8	9
Teb+ O_2								
20	80	86,1	13,9	4,00	6,19	0,164	0,94	1,22
50	50	72,6	27,5	1,00	2,64		1,00	1,64
60	40	65,6	34,4	0,67	1,91		0,59	0,80
70	30	61,2	38,8	0,43	1,58		0,41	0,56
80	20	61,0	39,0	0,25	1,56		0,20	0,44
90	10	54,2	45,8	0,11	1,18		0,06	0,10
Teb + Dps								
20	80	13,0	87,0	4,00	6,69	0,165	0,94	1,33
60	40	31,3	68,7	0,67	2,19		0,55	0,99
70	30	37,5	62,5	0,43	1,67		0,40	0,62
80	20	42,1	57,9	0,25	1,38		0,22	0,32
90	10	47,9	52,1	0,11	1,09		0,06	0,05
Dak								
50	50	27,9	72,1	1,00	2,58	0,066	0,85	1,35
60	40	34,0	66,0	0,67	1,94		0,78	1,10
70	30	39,1	60,9	0,43	1,56		0,64	0,83
80	20	44,6	55,4	0,25	1,24		0,43	0,42
90	10	47,6	52,4	0,11	1,10		0,15	0,13
[M_2]	[M_1]	[M_2]	[M_1]	[M_1]/[M_2]	[M_1]/[M_2]	A	Ξ	Η
1	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***

The Determination Of The Values Of The Relative Activities Was Carried Out Using The Graphical Dependences □ And □ (Fig. 27 A-C), From Which The Value □, Was Determined, Equal To The Value □ At □=0, The Value R_1 Corresponding To The Value □ At □=1 And The Value R_2= -□□.

Thus, In The Ba-Vbe Pair, The Relative Activities Of Ba In The Presence Of Various Initiators Were: Teb + O_2 (R_{ba} = 1.45 ± 0.07 And R_{vbe} ~ 0); Teb + Dps (R_{ba} = 1.51 ± 0.08 And R_{vbe} ~ 0); Dak (R_{ba} = 1.50 ± 0.08 And R_{vbe} ~ 0).

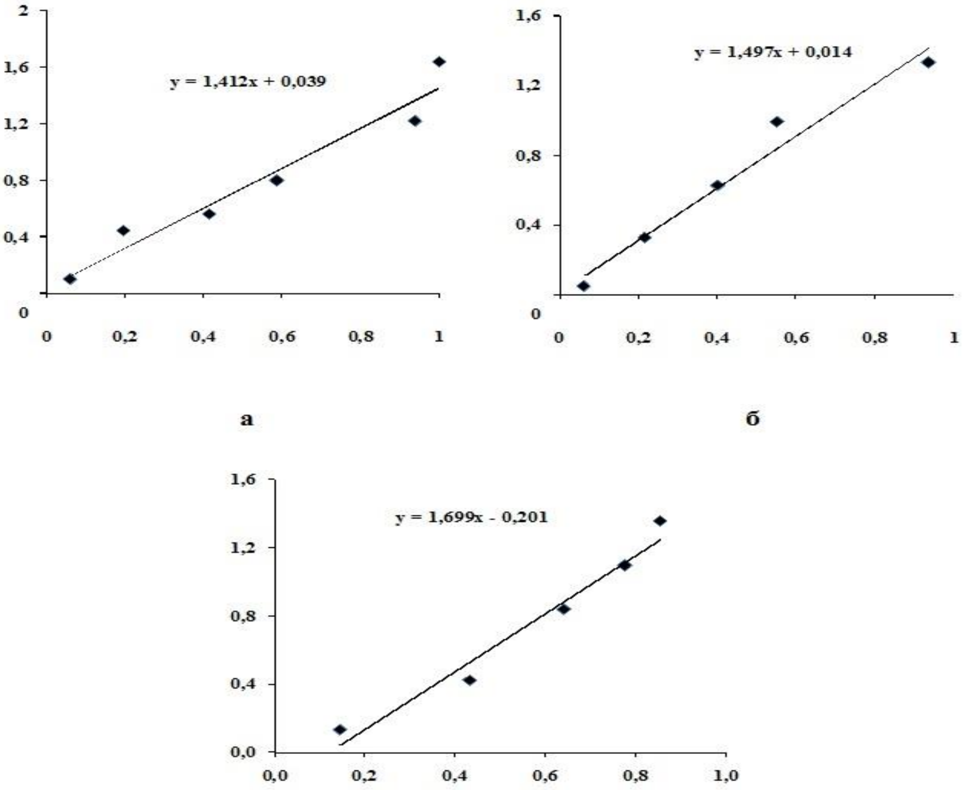


Fig. 1. Dependence Of □□On □□For Ba-Vbe Copolymers Obtained In The Presence Of A- Teb + O_2, B- Teb + Dps, And C – Dak.

Synthesis Procedure

Synthesis Of (Co) Polymers In Ampoules In The Presence Of Aibn

Samples Were Prepared For Bulk Polymerization Of Mma And St Monomers, As Well As For Ba-Vbe Copolymerization, As Follows: Exact Amounts Of Monomers And Initiator Were Placed In Glass Ampoules, Were Freed From Oxygen By Freezing The Reaction Mixture In Liquid Nitrogen And Pumping It Out To A Residual Pressure Of <1.3 Pa In A Vacuum Unit (Fig. 28).

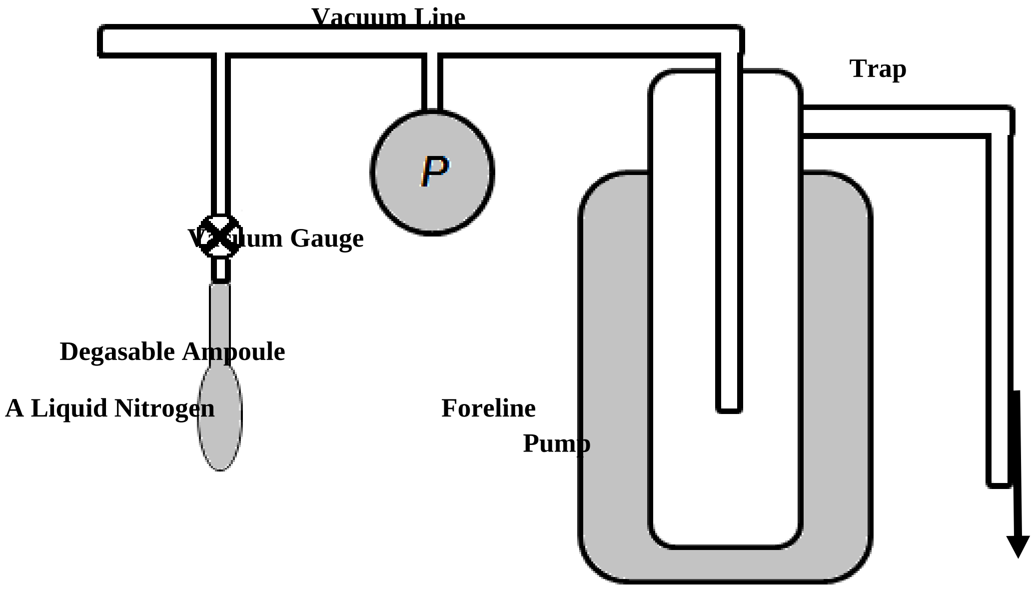


Fig. 2. Scheme Of A Vacuum Unit For Degassing Ampoules.

The Ampoules Were Sealed And Then Polymerized At A Strictly Defined Temperature. For This, The Ampoule Was Placed In A Thermostat For A Specified Time, After Which The Ampoule Was Removed And Frozen In Liquid Nitrogen To Interrupt The Polymerization.

In Order To Purify The Synthesized Copolymers From Residues Of Monomers, The Samples Were Transferred Into Weighed Glasses And Dried Under Reduced Pressure To Constant Weight. The Conversion Of Monomers Was Determined Gravimetrically, The Degree Of Conversion Was Calculated By The Formula:

$$P = M_s \times 100\% / (\sum M_m)$$

Where M_s – Copolymer Weight, G; $\sum M_m$ – Sum Of Masses Of Monomers, G;

Synthesis Of Copolymers In Ampoules In The Presence Of Organic Element Initiators

It Is Carried Out Similarly To The Synthesis In The Presence Of Dak, Except For The Stages Of Filling The Ampoules And Isolating The Synthesized Copolymers To Prevent The Uncontrolled Course Of The Reaction Due To The High Activity Of The Initiators.

The Ampoules Were Filled As Follows. We Used Exact Weighed Amounts Of Reagents. The Boramine Complex, Dissolved In Half Of The Monomer Mixture, Was Introduced Into An Ampoule, Frozen By Placing In A Vessel With Liquid Nitrogen. Then, Without Allowing Defrosting, The Second Half Of The Monomer Mixture With Maa (Or, Respectively, Maa + Dps) Was Introduced Into The Ampoule. Without Allowing The Reaction Mixture To Be Thawed, Excess Oxygen Was Freed By Pumping It Out To A Residual Pressure Of <1.3 Pa On A Vacuum Unit (Fig. 28) And The Ampoules Were Sealed. The Synthesis Of The Synthesized Polymers Was Carried Out Directly In The Ampoule. For This, The Frozen Ampoule Was Opened And, Gradually Heating, The Excess Of Unreacted Monomers Was Simultaneously Evacuated. Upon Termination Of The Drying Process, The Gravimeric Determination Of The Conversion Of Monomers Was Carried Out, And The Polymer Was Extracted By Dissolving In Chloroform And Transferring It To A Storage Container (Vials), Followed By Repeated Drying In A Vacuum Cabinet.

Synthesis Of Copolymers By The Compensation Method

The Synthesis Of Copolymers Was Carried Out In A Four-Necked Flask, Placed In A Thermostat, Equipped With A Reflux Condenser, Paddle Stirrer, Thermocouple, And A Branch For Injecting Reagents (Fig. 29). During A Series Of Experiments To Determine The Composition And Molecular Mass Of Copolymers, The Flask With The Monomer Mixture Was Immersed In A Hot Bath At A Predetermined Temperature.

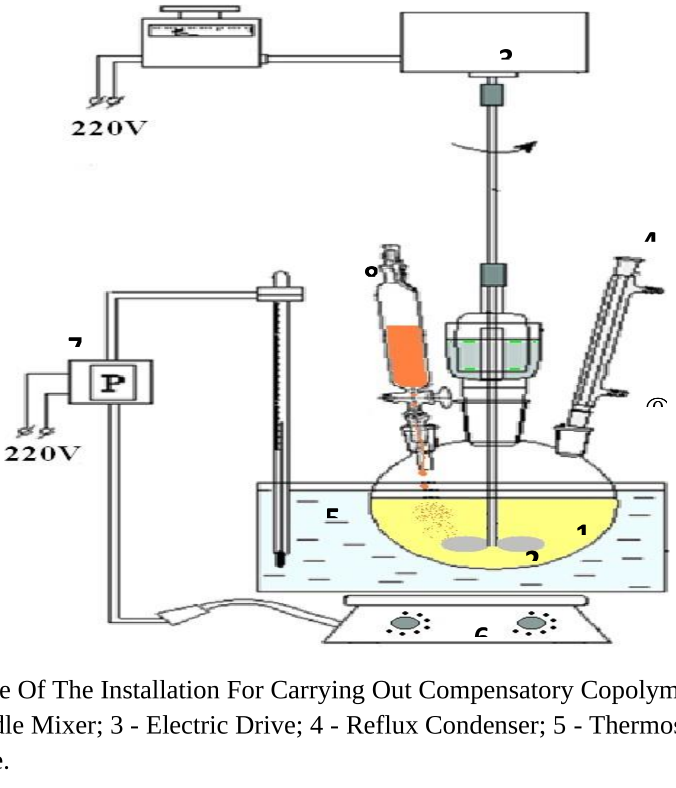


Fig. 3. Scheme Of The Installation For Carrying Out Compensatory Copolymerization In Boiling Monomer: 1 - Flask; 2 - Paddle Mixer; 3 - Electric Drive; 4 - Reflux Condenser; 5 - Thermostat; 6 - Heater; 7 - Thermal Relay; 8 - Dosing Device.

Determination Of Copolymer Composition By Ir Spectroscopy

The Ir Spectra Of The Synthesized Copolymers Were Recorded On A Shimadzu Ftir-8400s Ir Fourier Spectrophotometer In Kbr Cuvettes With An Optical Path Length Of 0.26 Mm In Chloroform Solution. The Range Of Wavenumbers Is 5500-550 Cm^{-1}, The Determination Error Did Not Exceed ± 0.05 Cm^{-1}. The Composition Of The Copolymer Was Determined Using A Calibration Graph Based On The Area Of The Characteristic Peak. The Absorption Spectra Bands Were Chosen As The Analytical Band: The Band At 1727 Cm^{-1} For The Carbonyl Group (Ama Fraction); Band At 1600 Cm^{-1} For C = C Vibrations Of The Aromatic Ring St (Fraction Of St). The Proportion Of Vbe Was Calculated As The Residual, Taking Into Account The Proportions Of Ama And St In The Copolymer.