Synthesis Study of Phosphonium Polymers with Unique Properties

Mukhamedgaliev BA[1*]
Palvuaniyazova DA[2]
Saburov HM[3]

[1]*Department of Building Materials and Chemistry, Tashkent Institute of Architecture and Construction, Tashkent State Technical University, Republic of Uzbekistan*

[2]*Department of Ecology, Karakalpak State University, Republic of Uzbekistan*

[3]*Department of Urban Construction and Economy, Tashkent Architecture and Construction Institute, Tashkent State Technical University, Republic of Uzbekistan*

Abstract

Nowadays an Epichlorohydrine [ECG] is widely used for the polymers synthesis, and its high reaction ability made it possible to synthesise some epoxy polymers [1,2].

The reactions of interaction ECG with amino-units are more studied [1,3] and as a result, the polymers with high reaction activity were received, which are used as superficial active substances, high-molecular stabilizers, polymer glues, etc.

In this aspect the reaction of interaction ECG with trivalent phosphorus units, which is the same according to structure of trivalent nitrogen, is much more interesting for study. We have studied the reaction of interaction ECG with triphenilphospin [TPP] which is less toxic.

Keywords: Polymer, Polymerization, Polyelectrolyte, Viscosity, Heat Resistance, Fire Resistance.

The Experimental part

The ECG before using was twice outrun (Boiling T=389 K, n_{fl}^{20}=1.4350; JI_n^{20}=l,1807). In IR-spectrum the line of absorbtion at 2870-3000 sm[1] 'is reliable to group (CH_2). The middle- intensively absorbing line in 850-800 sm[1]. is relating to the valents oscillation of CC1 structure group.

In PMR - spectrum the ECG is characterized by two multiplete signals at 2.5 and 2.75 m.p.

This is explained by the form of these signals which is the same with the signals in PMR spectrum of propilen oxide [4-6].

The multiplete complex signal situated in more weak fields with a centre 3.45 is reliable to the two proton metilen groups which are connected with chloride atom.

Triphenilphosphin is the white crystals recrystalized twice before using from the mixture of ethanol and diethyl ester.

There are some absorbed zones of weak activity in IR - spectrum.

IR -, PMR - and UV- spectroscopic investigations show that this product is a linear polymer, containing guarternary phosphonium groups in its external bonds.

$$CH_2 - CH - CH_2Cl + P(C_6H_5), \longrightarrow - CH_2 - CH - O - \quad (1)$$

Accordingly to potentiometric titration of the polymers water solution, the polymer contains chlor ions 10+1.0%, that is near the

theoretical content of chlor ions in polymer, received of equimolecular composition.

Thus the 1-st stage of the polymersization is Menshutkin reaction - the quarternization of TPP by epychlorhydrin.

For the investigation of TPP and ECG interaction the IR and UV-spectrums of the 1-st and final products were registered, so as PMR spectrum of the 1-st components, their mixtures during start and time.

In the polymer IR - spectrum, made on the basis of TPP and ECG interaction, the stripe of deformation oscillation P-Ph is in the low -frequent zone up to 1350 sm^{-1} in comparision with the zone in TPP- spectrum. This fact is explained by the low strength of P-Ph unit because of quarternizied phosphor.

The valent oscillation C- Cl unit (850 - 800 sm^{-1}) of ECG CH$_2$- group disappears because of formation new stripe in 1350 sm^{-1}, zone.

In the zone 1050 - 1100 sm^{-1} new intensive absorbtion stripes appear and they are the result of valent oscillation of the simple ester unit (C - O - C) because of the opening of epoxy – groups (1260,93 sm^{-1}) ECG during interaction with TPP. The stripe in the zone of 930 sm^{-1} is partially reserved, characterizing epoxy -groups, that was proved by the definition of epoxy number which was equal to 1,18 according to the method [7].

In PMR - spectrum of the polymer the signals of phosphonium benzene rings protons appear by 7,80 m.d. as a multiplete and protons of the qroups O - CH$_2$ -CH and P$^+$-CH$_2$ ECG as a multiplete with a centre 3,8 m.d. The groups of multiplete signals by 2,33 m.d. probably because of the polymer chains formation, in which CH and CH$_2$ groups are more shield than in the first components. The ratio charge of the protons signals of benzene and non - benzene rings is about 1:2,2, that practically corresponds to the proposed structure.

The presence of quarternary phosphonium group in the polymer structure was proved by UV - spectrum. So in the zone of 240 - 260 nm there are absorption stripes which are typical for the quarternary phosphonium group. The spectrum investigation shows that the beginning of TPP and ECG interaction is the quarternization (Menshutkin reaction which involves the epoxy cycle into this one and the opening of this process leads to the receiving of the linear polymers. What is the mechanizm of this process?

The kinetic regularity of TPP and ECG interaction by dilatometrical method was received. It is proved, that efflctive ingibitors of the radical polymerization such as hydroquinone, air oxygen, stable imine oxide radicals, 2.2.6.6 -tetramethylpiperidine - 1 - oxide don't influence on the polymerization speed and that proves the non - radical character of the process. In EMR - spectrum of TPP and ECG system with different conditions the formation of radical is not seen. The influence of solvent nature on the starting speed of TPP and ECG interaction has been studied.

The investigations were made taking into account the homogeneity of the medium. The results showed that the more the solvent dielectric penetrability the more

the reaction speed figure 3 and that is connected with the increasing of Menshutkin reaction which is the first stage of the process

The study of the temperature influence on the interaction velocity of TPP and ECG proves that the temperature which is move than 10° increases the interaction velocity in 3 times, and its dependence on the temperature is under the meaning in accordance with Arenius equation. The effective energy of activation in accordance with the table in ethanol is 12,79 kkal / mol, that is the same with the activation energy according to Menshutkin reaction and is the 1-st stage of the process. So we may suppose that Menshutkin reaction is the limited stage of the process.

On the basis of the experimental results [8,9] we may suppose the following interaction scheme of ECG with TPP. The atom of ECG haloid makes connected with it carbon of chlormethyl group the place of the first nucleophilic attack and the 1-st stage of the process is the quarternization reaction (Menshutkin reaction):

$$CH_2 - CH - CH_2Cl + P(C_6H_5), \longrightarrow CH_2 - CH - O - \\ \backslash \; / \qquad\qquad\qquad\qquad\qquad\quad | \\ O \qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2 \\ (2) \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ (C_6H_5)_3P^+Cl^-$$ (2)

As a result of electron density moving in the quarternization molecular the tense of three nominal cycle becomes low and under the pressure of anione haloid active ion pair of oxirane cycle the opening reaction of the polar carbon - oxygen link is taken place.

$$CH_2 - CH \qquad\qquad Cl - CH_2 - CH - 0 \\ \backslash \; / \; | \qquad\qquad\qquad\qquad\qquad | \\ 0 \;\; CH_2 \qquad\qquad\qquad\qquad\quad CH_2 \\ (C_6H_5)_3P^+Cr \qquad\qquad\qquad (C_6H_5)_3P^+$$ (3)

The quarternization and the opening reaction are the stages influencing on velocity according S$_N$2.

The chain growing is according to anione polymerization while acting particle and then with dimer and trimer, etc.

$$Cl-CH_2-CH-0 + CH_2-CH \;\rightarrow\; Cl-CH_2-CH-0- CH_2 - CH - CH \\ 0 \; | \qquad\qquad | \qquad\qquad\qquad\qquad | \qquad\qquad | \\ CH_2 \qquad CH_2 \qquad\qquad\qquad CH_2 \qquad CH_2 \\ (C_6H_5)_3P^+ \quad (C_6H_5)_3P^+Cr \qquad (C_6H_5)_3P^+Cr \quad (C_6H_5)_3P^+$$ (4)

The chain break is taken place probably because of acting equimolecular substances or by adding of the solvent proton with macroanione according to schemes

$$CL-CH_2-CH-O- CH_2 - CH \quad O- CH- \\ | \qquad\qquad | \\ CH_2 \qquad\qquad CH_2 \\ | \qquad\qquad | \\ (C_6H_5)_3P^+ \qquad (C_6H_5)_3P^+CL^-$$ (5)

For the experimental test of the received kinetic scheme, the kinetic order regularities of the interaction TPP and ECG were investigated. The results are shown in table 1

So on the basis of kinetic data table 1 of TPP and ECG interaction the reaction order was determined according to components which are equal 1,1 and 0,88 correspondingly, so as the general order of reaction which is equal 1,9. The summary 2 - nd order and the components order, which is near 2, confirm our suggestion about bimolecular substitution

No	[ECG]m ol/l	TFF mol/1	$v \cdot 10^6$ mol 1 c	$-6+lg^v$	n ndl / r	reaction order n
1	0,5	0,05	0,62	0,79	0,105	
2	0,5	0,075	1,17	1,06	0,122	1,1
3	0,5	0,1	2,06	1,31	0,183	
4	0,5	0,125	3,17	1,47	0,21	
5	0,25	0,5	4,66	0,66	0,247	
6	0,5	0,5	9,83	0,962	0,18	0,88
7	0,75	0,5	12,10	1,04	0,166	
8	1,00	0,5	17,3	1,23	0,131	
9	0,25	0,25	3,07	0,127	0,342	
10	0,5	0,5	9,83	0,962	0,122	1,9
11	0,75	0,75	17,71	1,27	0,118	
12	1,00	1,00	39,28	1,59	0,117	

Table 1: The dependence of the starting velocity of the process TPP and ECG interaction on the components concentration. T = 323 K, ethanol.

reaction. The equation of general polymerization ECG and TPP is the following :

$$V_{common} = K_{common} \; [ECG] \quad [TPP] \; '$$

This equation is the same as in Menshutkin reaction, which is limited stage of polymerization process, except the difference in reaction order by monomer. The highest meaning of the order proves that with quarternarized chains of ECG there are non-quarternarized chains. This is confirmed by study of IR - spectres of polymers received during ECG and TPP intereaction and we see that the absorbing zone is not disappeared absolutely at the level of 850 -- 880 sm, relating to the deformation oscillation C-Cl-group.

The difference in the Cl-ion meanings, detennined by potentiometric titration (Cl - 10,01 %) in comparison with the element analysis (Cl = 13,6 %) is also proves our suggestion.

$$—O\text{-}CH_2\text{-}CH — \quad O\text{-}CH_2\text{-}CH — CH_2Cl$$

$$\underset{(C_6H_5)_3 \; P^+Cl \quad n}{\overset{CH}{|}} \tag{6}$$
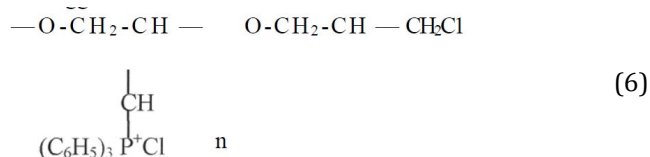
This is explained by the following together with Zwitter-ion polymerization there is anionic polymerization of the non- quarternarized ECG molecules with the opening of high - polar carbon - oxygen chain of the epoxy cycle as oxides olefines. Thus the synthesized polymer is a powder of brown colour, stable to long storage with 428 K, the density determined by pycnometer method is 1,388 g/sm³, it is solved in dymethilphormamid, ethanol, methanol, water and in the other polar solvents. The study of viscosity proved that it is the typical polyelectrolyte and the dependence of c/n from c for water solvents of the synthesized polyelectrolytes is of linear character which proves that water solvents behavior is described by Fuoss - Strauss equation [10].

The dependence of polymer solution viscosity on the concentration of phosphonium polymers in the presence of strong electrolyte 0,25 KC1 solution is of straight - line character, because of creation screen "fur coat " anti-ions around macromolecular ions. The polymers obtained in various conditions are also heat resistant. The Vicat heat resistance of a polymer based on ECG with TPP synthesized in ethanol at T = 333K - 406K of the same polymers and at T = 303K, respectively - 420K. The flow temperature of the

latter polymers is also high — 497K and 481K, while the polymers synthesized at T = 333K are 467K, respectively. An increase in the thermal and heat resistance of the polymer is associated with the formation of highly ordered structures under the conditions of spontaneous polymerization at a relatively low temperature.

The molecular weight and molecular weight distribution (MWD) of polymers obtained on the basis of the interaction of ECG with TFF was determined by the method of speed sedimentation and viscometry, since speed sedimentation is the simplest and most accessible method of sedimentation analysis of polymers of practical interest. Determination of molecular weight by sedimentation rate is based on the use of sufficiently large accelerations, providing such a rate of sedimentation of molecules that can be measured. The advantage of this method is the high sensitivity of the parameters obtained in the experiment to the degree of heterogeneity of the drug according to molecular masses, with this you can get an idea of its purity and quantitative data on the degree of polydispersity, calculate the sedimentation constant and molecular weight of polymers, find out the possibility of various transformations of macromolecules associated with conformational shape changes. The sedimentation coefficient, as well as the characteristic viscosity, at a certain molecular weight depends only on the size and shape of the macromolecules.

Therefore, studying the dependence of the characteristic sedimentation constant on temperature and solvent composition, one can obtain information on the conformational transformations of macromolecules in solutions. The polydispersity index M_w/M_n was calculated directly from the sedimentation diagrams using an approximate method [8,11] based on the established relation linking the sedimentation coefficient S01 to the MM fraction. The research results are summarized in table 2.

Extrapolation of the sedimentation coefficient to infinite dilution shows that at low concentrations of dissolved polymer, the constant Ks for a fairly wide range of molecular weights can be represented with sufficient accuracy as a product of Ks S0. In addition, in most cases, the value of Ks, in the relation S = S0 (1-KsC) is positive, i.e. when diluted S increases. This position is not surprising, since for many linear polymers, it is shown that the value of Ks is proportional to the characteristic viscosity of the polymer, and in ideal

No	The polymers obtained with equimolar. components of output,	Tempera-ture, K	Output,%	η reduced viscosity dl/g	V 10^6 mol/l s	Mn*10^{-3}	M$_w$/M$_n$
1.	ECG : TPP *	268	71,2	0,268	0,120	56	1,2
2.	ECG : TPP *	273	67,9	0,262	0,314	55	1,3
3.	ECG : TPP *	293	66,4	0,26	0,68	53	1,5
4.	ECG : TPP *	303	63,0	0,25	1,42	52	1,7
5.	ECG : TPP [1]	313	61,3	0,24	2,73	51	1,8
6.	ECG : TPP [1]	318	56,1	0,22	4,04	47	2,3
7.	ECG : TPP [1]	323	52,4	0,20	6,72	41	2,5
8.	ECG : TPP [1]	333	48,2	0,19	15,15	36	2.6

Table 2: The effect of polymerization conditions on the molecular mass characteristics of phosphonium polymers in ethanol (*) and DMF (').

conditions [η] is proportional to the sedimentation constant.

During the experiments, a strong diffusion effect was found for both the unfractionated samples studied, which is probably due to the rather low values of sedimentation coefficients.

Figure 1,2

By constructing the dependence of LgSo on LgM, we found constants in the Flory-Mandelkern equation for phosphonium polymers in ethanol at 298 K table 2.

As can be seen from the data presented in table 2. with increasing polymerization temperature, under other constant conditions, the molecular weight of phosphonium polymers decreases, the Mw / Mn increases and the solubility deteriorates. The decrease in the yield of polymers appears to be associated with a decrease in the concentration of effective active centers and an increase in the rate of growth of molecular chains at these centers caused by an increase in temperature should contribute to an increase in the proportion of molecules with high molecular weight.

In addition, with increasing polymerization temperature, the role of chain restriction reactions increases, the temperature coefficient of which is higher than that of chain growth reactions. As a result, in all likelihood, the proportion of low molecular weight fractions in polymers increases.

There is a direct connection between the viscosity and the form of the macromolecule in the solution. Therefore, of particular interest is the study of viscosity in mixed solvents. It has been established that with an increase in the content of ethanol and dimethylformamide in the mixture, the viscosity decreases, but at the same time a dependence characteristic of polyelectrolytes is observed. According to the results of experiments, dimethylformamide effectively reduces the viscosity of aqueous solutions of phosphonium polymers than ethanol, i.e. polymeric macromolecules in dimethylformamide coagulate more than in ethanol.

Determination of viscosity in mixed solvents suggests that when the solvent composition changes, the structured formations of polymer macromolecules are destroyed. The greatest influence on the conformation of macromolecules in solutions is exerted by a change in the concentration of hydrogen ions, which is associated with a change in the charge and hydration of the macromolecules. As a result, the dependence of the viscosity of the synthesized phosphonium polymers on pH is complex. The viscosity of 0.1% aqueous solutions of phosphonium polymers based on ECG with TPP with a pH increase passes through a maximum figure 3. To a pH of 5.5, a slow increase in viscosity occurs, and then a steep rise in the dependence of η s / C on pH begins. The maximum is usually achieved with full neutralization of functional in the case of phosphonium polymers based on ECG and TPP having a higher viscosity. With complete neutralization, as well as with an excess of alkali, the dependence of water flow ratio on the pH decreases. In the neutral pH range, the size of macromolecules of phosphonium polymers is greatly increased.

The picture of the change in the dependence of η/C on pH reflects the state of the polymer in solution: the lowest pH values are characterized by the maximally curtailed types of structures formed because of the interaction of macromolecules of phosphonium polymers and due to the complete screening of charges when electrolyte is added [12,13]. As the screening of charges on the macromolecule and hydration decrease, these structures swell and unfold, which is accompanied by a sharp increase in viscosity.

This is fixed by the maximum value on the viscosity curve, which decreases with a lower degree of ionization, which indicates the beginning of the disintegration of aggregates of macromolecules. With the further introduction of alkali, it appears that the screening effect of the charge of the phosphonium polymer macromolecule reappears and the dissociation of the polyelectrolyte is suppressed, which naturally leads to a decrease in viscosity.

The molecular mass of polymers was determined by the method of high - speed sedimentation using the equation of
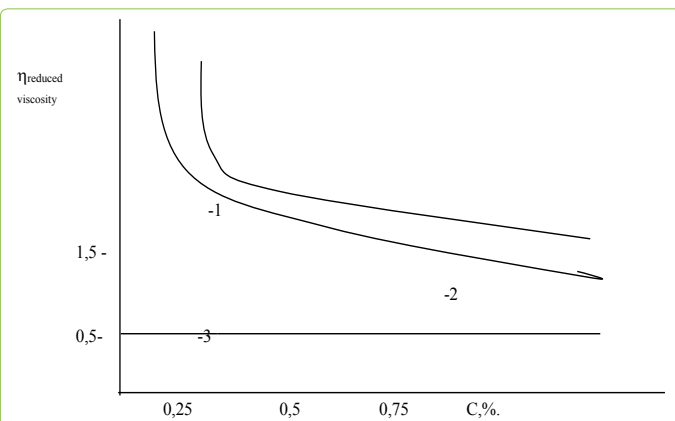
Figure 1: 1 - dependence of reduced viscosity on polymer concentration in water, 2- dependence of reduced viscosity on polymer concentration in a mixture of water + ethanol, 3- dependence of reduced viscosity on polymer concentration in a 0,25N KCl solution.
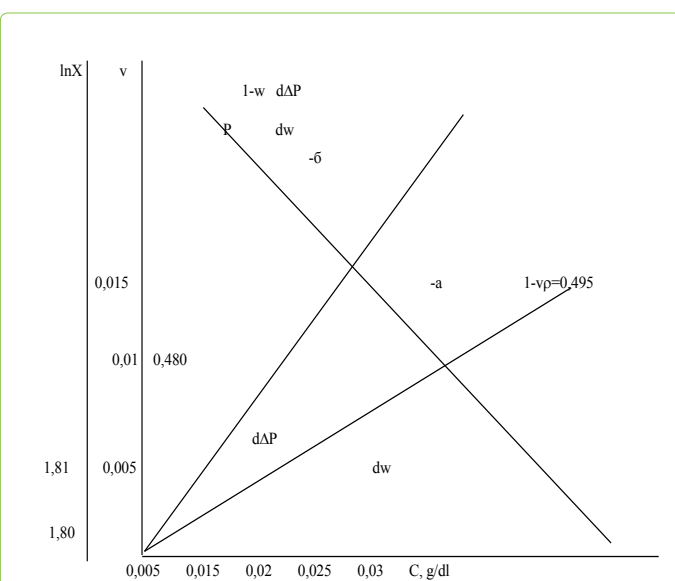
Figure 2: Determination of the molecular weight of the polymer based on ECG and TPP. a) determination of sedimentation coefficient; b) determination of partial-specific volume.
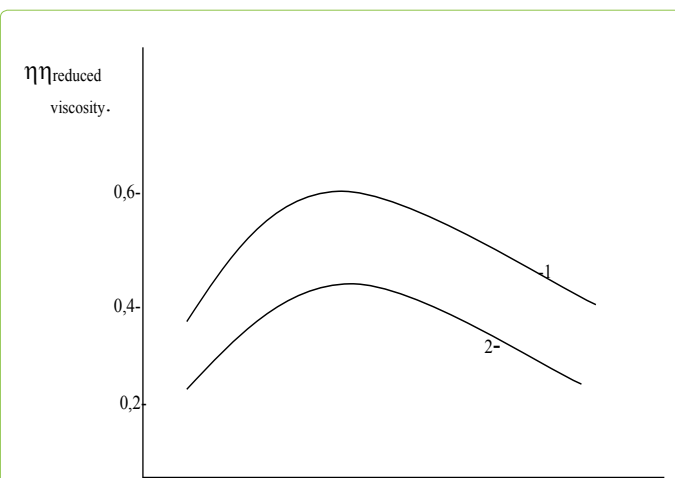
Figure 3: Dependency $\eta\eta$пр. pH for 0.1% aqueous solutions of phosphonium polymers. 1-polymer based on ECG and TFF, 2- polymer based on Methacrylchloride (MAX) and TFF.

Flory -Mandelkern which was equal to 51000.

Thus on the basis of kinetic, spectral and chemical methods was studied the reaction of interaction ECG and TPP and supposed polymerization process was shown, that is able to receive the catione polyelectrolyte, contained in the side chains the quarterized groups.

The obtained research results were the basis for the development of the technology for the production of phosphonium polymers, the peculiarities of which are the carrying out of the polymerization process by a periodic method. The features of the developed technology are simplicity in technological design, high efficiency of technological processes. The polymers obtained by the developed technology are more homogeneous in molecular weight and, therefore, have a lower degree of polydispersity.

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