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Special topic

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Synthesis of inorganic polymers under ionizing and super high frequency irradiation: role of reaction media

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Abstract: This article provides a general overview of the results of research on the influence of the reaction media and various types of electromagnetic radiation on the polymerization of inorganic monomers, carried out during the last decade at UNESCO Chair in Green Chemistry for Sustainable Development of Dmitry Mendeleev University of Chemical Technology of Russia.

Keywords: Distinguished Women in Chemistry and Chemical Engineering; elemental phosphorus; elemental sulfur; ionic liquids; ionizing irradiation; reaction media; super high frequency irradiation.

Introduction

A study of the processes that take place during the polymerization of inorganic monomers [e.g. elemental (white) phosphorus and sulfur] under the influence of various types of radiation was undertaken by the UNESCO Chair in Green Chemistry for Sustainable Development (former Department for the Problems of Sustainable Development) of Dmitry Mendeleev University of Chemical Technology of Russia, over the course of more than 20 years. This period was characterized by a significant growth of the interest in green technology in general, and in green chemistry in particular. One of the most remarkable methods of implementation of green chemistry is the design and the investigation of new solvents, among which ionic liquids (ILs) are worthy of mention. ILs have many unique properties that are beneficial in polymerization processes, justifying our interest in these substances. An overview of our research in this field over the past decade is presented herein, along with the noteworthy data from other studies.

Ionic liquids in the radiation-chemical synthesis of phosphorus-containing polymers

The initial objective of this study was to improve the method of synthesis of polymeric phosphorus (i.e. widely used red phosphorus [1–3]) with various dopants, namely, phosphorus-containing polymers (PCPs). The approach involved finding ways to lessen the environmental impact (high pressure and temperature, and toxic wastes) of existing technologies for the production of red phosphorus. White phos-

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phorus is highly reactive, flammable, and toxic. Thus, the radiation-induced synthesis of PCPs under various conditions was studied to design a process that meets the principles of green chemistry [4, 5]. In these studies, imidazolium- and pyrrolidinium-based ILs (low-toxic solvents) were used as components of the reaction media (principles nos. 4 and 5). In the past decades, a significant number of studies dealing with ILs in the context of the principles of green chemistry has been published, where ILs are considered as a potential alternative to volatile organic solvents [6]. ILs exhibit many useful properties, including non-flammability, thermal stability, high electrical conductivity, ionic character, low vapor pressure, etc. Moreover, the variability of the component cations and anions makes it possible to "tune" the properties of ILs over a wide range [6–16]. For example, the solubility of elemental phosphorus in ILs was reported to depend on the IL structure [17]. ILs can be used not only as a solvent, but also as a catalyst [18] and a stabilizing medium [6].

In our research on PCPs, the addition of an IL was found to lead to high product yields and high selectivity of the reaction without intermediate transformations (principles nos. 2, 8, and 9). Carrying out the process at room temperature and atmospheric pressure permitted a decrease in the environmental energy impact (principle no. 6). In addition, the solvents are stable under irradiation and could be recycled after separation of the PCPs (principle no. 7).

The reaction rates and apparent rate constants were found to strongly depend on the structure and the concentration of the IL in the reaction medium. Therefore, in subsequent studies, attempts were made to control the radiation-chemical processes by adding various ILs. To this end, imidazolium- and pyrrolidinium-based ILs were used as before, and phosphonium-based ILs with similar alkyl chains were also employed [19]: $\mathrm{[BuMeIm]CF_3SO_3}$, $\mathrm{[BuMeIm]BF_4}$, $\mathrm{[BuMeIm]PF_6}$, $\mathrm{[EtMeIm]N(SO_2CF_3)_2}$, $\mathrm{[BuMePyr]N(SO_2CF_3)_2}$, $\mathrm{[HeMeIm](C_2F_5)_3PF_3}$, $\mathrm{[Et_3OcP]N(SO_2CF_3)_2}$, $\mathrm{[Et_3DdP]N(SO_2CF_3)_2}$, $\mathrm{[Bu_3MeP]N(SO_2CF_3)_2}$, $\mathrm{[Bu_3OcP]N(SO_2CF_3)_2}$, $\mathrm{[Bu_3DdP]N(SO_2CF_3)_2}$, $\mathrm{[Bu_3OcP]BF_4}$, $\mathrm{[Bu_3DdP]BF_4}$, $\mathrm{[Bu_3MeP](CH_3)_2PO_4}$, $\mathrm{BuMe_2Im]BF_4}$ (Table 1).

In the experiments, elemental phosphorus was dissolved in a dimethyl sulfoxide (DMSO)–benzene (1:1) mixture with addition of the IL ($[\mathrm{IL}] = 0.1–0.2$ M for different ILs), and the mixture was irradiated with $^{60}\mathrm{Co}$ γ-radiation (dose rate $P = 0.59$ Gy s^{-1}, ferrous sulfate dosimetry system [20]) at 298 K. Benzene was chosen as the main component of the reaction medium due to its high radiation resistance and high phosphorus (and sulfur) dissolving ability, despite the fact that benzene is a volatile organic compound. The reaction products (PCPs) were characterized by elemental analysis, infrared (IR) spectroscopy (Bruker Tensor 27M), X-ray diffraction (XRD; DRON-3M diffractometer), and scanning electron microscopy (SEM; Tesla BS 340).

The elemental analysis and IR spectroscopy data were typical for PCPs [21] prepared in benzene via a similar experimental procedure [composition – P: 67–70 wt.%; C: 6–7 wt.%; H: 1.8–2 wt.%; and O: <20 wt.%; chemical bonds – P–O–H (1460 cm^{-1}), P–O (1380 cm^{-1}), P–H (1150 and 970 cm^{-1}), and P–C (720 cm^{-1}), P–P (weak absorption band at 500 cm^{-1})] [22, 23].

The apparent reaction rate constants (k) for the polymerization were calculated from kinetic analysis of the residual concentration of elemental phosphorus in the reaction mixture during the process of irradiation (iodine titrimetry [24, 25]). The analysis demonstrated the strong effect of the nature of the IL on the rate and the energy efficiency (radiation-chemical yield) of the radiation-chemical process. After addition of the IL, the radiation-chemical yield increased by two orders of magnitude compared to that of the process without ILs. This may be attributed to the formation of IL–$\mathrm{P_4}$ complexes, structurization of the elemental phosphorus solutions by the ILs, or the increased role of ion-radical processes (generally, radiation-induced polymerization of white phosphorus proceeds via the radical mechanism).

The formation of IL–$\mathrm{P_4}$ complexes may occur via weak interactions in the aromatic solvent (benzene), as suggested by $^{31}\mathrm{P}$ NMR data and quantum-chemical calculations for the $\mathrm{P_4}$–$\mathrm{C_6H_6}$ system [26–28]. The structurization and the formation of nanoaggregates of white phosphorus may be induced by the addition of amphiphilic compounds (ILs) to the solution [29–33]. Some investigations have reported liquid clathrates [33] and tube-like structures with a rectangular cross-section around the IL cations [34] in benzene–IL systems. Ion-radical processes may be important for ion aggregation [35]. Notably, the described processes

Table 1: List of ILs with abbreviations and structures of cations and anions.

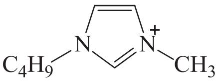
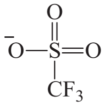
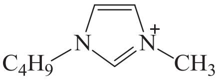
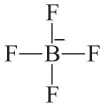
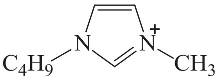
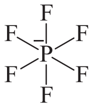
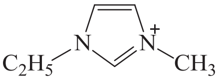
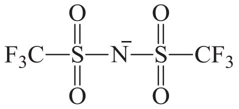
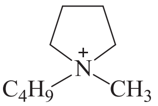
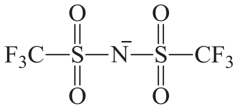
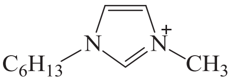
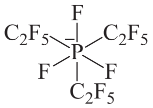
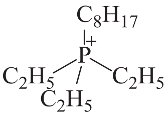
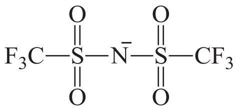
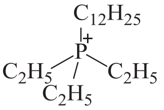
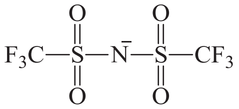
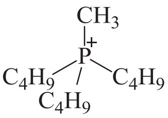
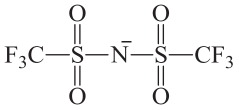
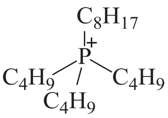
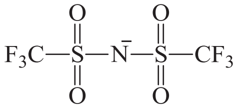
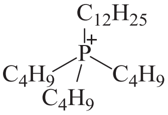
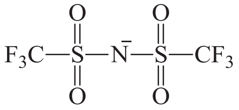
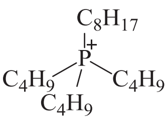
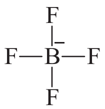
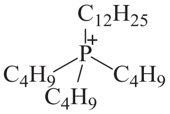
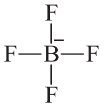
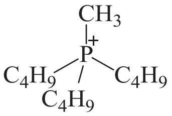
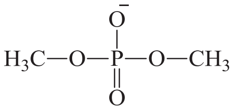
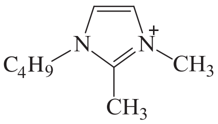
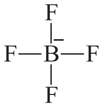
IL	Abbreviation	Cation structure	Anion structure
1-Butyl-3-methylimidazolium trifluoromethanesulfonate	[BuMeIm]CF_3SO_3		
1-Butyl-3-methylimidazolium tetrafluoroborate	[BuMeIm]BF_4		
1-Butyl-3-methylimidazolium hexafluorophosphate	[BuMeIm]PF_6		
1-Ethyl-3-Methylimidazolium bis(trifluoromethylsulfonyl) imide	[EtMeIm]$N(SO_2CF_3)_2$		
1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide	[BuMePyr]$N(SO_2CF_3)_2$		
1-Hexyl-3-methylimidazolium tris(pentafluoroethyl) trifluorophosphate	[HeMeIm]$(C_2F_5)_3PF_3$		
Triethyloctylphosphonium bis(trifluoromethylsulfonyl) imide	[Et_3OcP]$N(SO_2CF_3)_2$		
Triethyldodecylphosphonium bis(trifluoromethylsulfonyl) imide	[Et_3DdP]$N(SO_2CF_3)_2$		
Tri-*n*-butylmethylphosphonium bis(trifluoromethylsulfonyl) imide	[Bu_3MeP]$N(SO_2CF_3)_2$		
Tri-*n*-butyloctylphosphonium bis(trifluoromethylsulfonyl) imide	[Bu_3OcP]$N(SO_2CF_3)_2$		
Tri-*n*-butyldodecylphosphonium bis(trifluoromethylsulfonyl) imide	[Bu_3DdP]$N(SO_2CF_3)_2$		
Tri-*n*-butyloctylphosphonium tetrafluoroborate	[Bu_3OcP]BF_4		

Table 1: (Continued)

IL	Abbreviation	Cation structure	Anion structure
Tri-*n*-butyldodecylphosphonium tetrafluoroborate	$[Bu_3DdP]BF_4$		
Tri-*n*-butylmethylphosphonium dimethylphosphate	$[Bu_3MeP](CH_3)_2PO_4$		
1-*n*-Butyl-2,3-dimethylimidazolium tetrafluoroborate	$[BuMe_2Im]BF_4$		

proceed efficiently in the presence of imidazolium ILs, but this is not the case in the presence of phosphonium ILs as the latter can trap the solvated electrons [36] and inhibit the process of white phosphorus polymerization.

During polymerization, the tetraphosphorus molecule behaves in a manner similar to an olefin molecule [37], and the efficiency of olefin polymerization in the presence of ILs is almost independent of the IL cation type [38].

All these facts lead to a complicated dependence of the apparent rate constant of the described processes on the IL concentration and nature, as observed for $[BuMeIm]CF_3SO_3$, $[BuMeIm]BF_4$, and $[BuMeIm]PF_6$ (Fig. 1), and $[EtMeIm]N(SO_2CF_3)_2$, $[BuMePyr]N(SO_2CF_3)_2$, and $[HeMeIm](C_2F_5)_3PF_3$ (Fig. 2).

These phenomena could be the consequence of structural reorganization in the solution, caused by the structural characteristics of the IL, whereas the direct action of high energy radiation on the IL is negligible because of the low electronic fraction of the IL (<0.1).

The appearance of IL–P_4 structures and interaction between the reagents and radiolysis intermediates result in a change of the kinetic order of the reaction of white phosphorus from first to second order [5, 21].

Among the primary products of radiolysis (solvated electron, hydrogen atom, hydroxyl radical), the reaction between the IL and solvated electron is the most probable.

If the initiation of white phosphorus polymerization proceeds via this reaction, it is important to assess the steric factor, e.g. comparing the cross-sectional area, *S*, of the IL molecule and the IL–P_4 complex (Table 2), which is proportional in the first approximation to $V^{2/3}$ (V – molar volume of the IL).

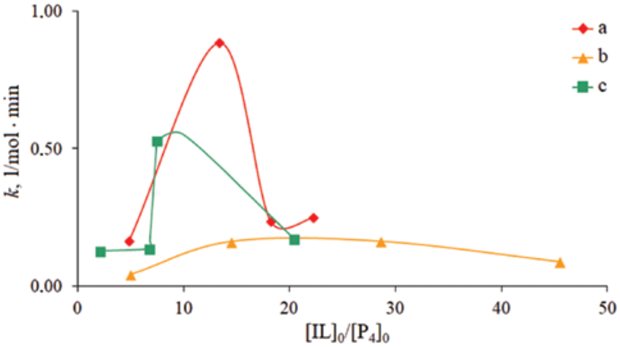


Fig. 1: Dependence of the apparent reaction rate constant of white phosphorus polymerization (*k*) on the ratio of the reagents (T = 298 K, P = 0.59 Gy s^{-1}): (a) $[BuMeIm]CF_3SO_3$, (b) $[BuMeIm]BF_4$, and (c) $[BuMeIm]PF_6$.

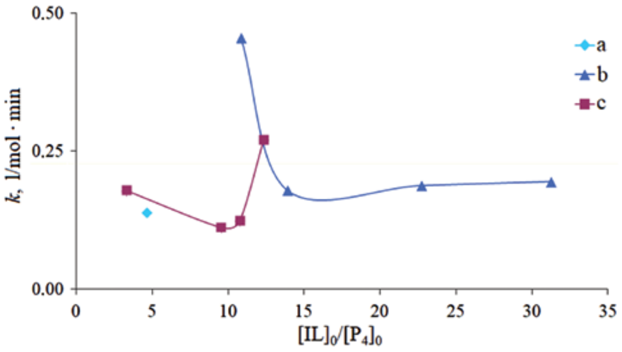


Fig. 2: Dependence of the apparent reaction rate constant of white phosphorus polymerization (*k*) on the ratio of the reagents ($T = 298$ K, $P = 0.59$ Gy s^{-1}): (a) [EtMeIm]CF_3SO_3, (b) [BuMePyr]$N(SO_2CF_3)_2$, and (c) [HeMeIm]$(C_2F_5)_3PF_3$.

Table 2: Apparent rate constants (*k*) and cross-sectional areas (*S*) of imidazolium ILs.

IL	*k*, l/(mol · min) for $[IL]_0/[P_4]_0 = 10$	$S \sim V^{2/3}$, nm^2
[BuMeIm]BF_4	0.12	0.47
[BuMeIm]PF_6	0.45	0.49
[BuMeIm]CF_3SO_3	0.63	0.52
[BuMePyr]$N(SO_2CF_3)_2$	0.50	0.62
[HeMeIm]$(C_2F_5)_3PF_3$	0.12	0.75

In the case of the same cation ($[BuMeIm]^+$), an increase in the cross-sectional area corresponds to an increase in the apparent rate constant. This is attributed to structural changes in the reaction medium due to trapping of the active intermediates by the IL molecules.

Thus, we assumed that the concentration of white phosphorus in these systems could fluctuate due to solvation interactions. The effect of the IL, as a component of the reaction medium, on the reaction parameters (e.g. apparent rate constant) allows “fine tuning” of the process, which is very important for green chemical technology.

The processes involving the phosphonium and imidazolium/pyrrolidinium ILs demonstrated several peculiarities. Thus, the decision was made to investigate the system with $[Et_3OcP]N(SO_2CF_3)_2$ in detail [39].

PCPs were synthesized based on white phosphorus in the propan-2-ol–benzene–IL system (benzene:propan-2-ol molar ratio 6.5:1, [IL] = 0.1–0.2 M for different ILs) under ^{60}Co γ-radiation at 298 K. The reaction products (PCPs) were characterized by elemental analysis, X-ray photoelectron spectroscopy (XPS), IR spectroscopy (Bruker Tensor 27M), XRD (DRON-3M diffractometer), SEM (Tesla BS 340), transmission electron microscopy (TEM), and ^{31}P and ^{1}H NMR spectroscopy. The characteristics of the PCPs (Fig. 3) were similar to those of commercial red phosphorus and previously synthesized samples [5, 40]. The present PCP samples, as well as that synthesized in pure benzene solution (reference sample), was X-ray amorphous. The average size (0.25 µm) was much smaller than that of the reference sample (11 µm), plausibly due to the decreased solubility of PCP in the polar solvent propan-2-ol–benzene–IL as compared to that in pure benzene.

The elemental composition of the PCP sample was similar that of previously synthesized samples – P: 56 wt.%; C: 6 wt.%; H: 3 wt.%; and O: ~35 wt.% (possible chain termination by organic radicals results in the chemical incorporation of benzene fragments and leads to the presence of C and H in the sample; the presence of oxygen is also the result of the incorporation of oxygen-containing organic radicals that initiate the polymerization or the result of partial oxidation of the sample surface). The high content of C (68 wt.%) in the surface layers (as determined by XPS) results from sorption of the solvent molecules on the surface of the PCP particles.

SEM and TEM imaging showed the presence of spherical and elliptical particles in the PCP sample, with sizes of 10–140 nm; about 45 % of the nanoparticles were 30–50 nm in size.

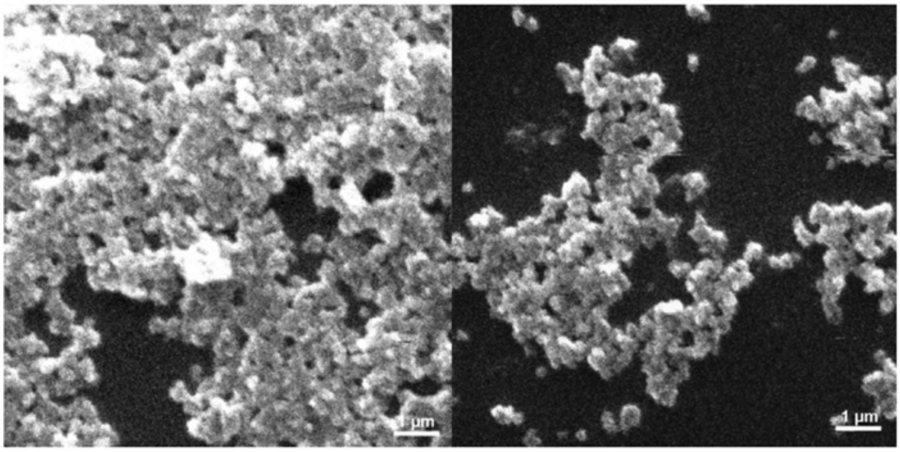


Fig. 3: Micrographs of PCP synthesized in propan-2-ol–benzene–IL. $T = 298$ K, $P = 0.59$ Gy s^{-1}, $D = 24.7$ kGy, $[P_4]_0 = 0.013$ M, and $[IL]_0 = 0.16$ M.

The IR spectra indicated P–P bonds (490–520 cm^{-1}) [21, 22] and inclusion of the benzene organic fragments in the resulting polymer (1400 and 1010 cm^{-1}) [41]. The other bonds were similar to those described above.

The ^{31}P NMR spectra of the PCP samples demonstrate the presence of the following bonds: P–Ph (~0 ppm), P–H (7 ppm), O=P–H or HO–P–H (16 ppm), polymeric P–P (~30 ppm) [42, 43], and that of white phosphorus P–P (–450 (–460) ppm) [1, 22, 43]. The ^{1}H NMR spectra demonstrate the presence of the following bonds: C_{Ph}–H (7.7 ppm), P–H (5.1 ppm), and P(O)–H (4.8 ppm).

As mentioned above, white phosphorus is a rather hazardous substance; at the same time, it is a very important reagent in organophosphorus synthesis. Thus, the synthesized PCPs were tested at A. E. Favorsky Institute of Chemistry of Russian Academy of Sciences, Siberian Branch (Irkutsk) by evaluating the interaction between PCP and α-methylstyrene in a superbasic medium (the Trofimov-Gusarova reaction, Fig. 4, at 393 K for 3 h in KOH–DMSO [40].

The products of this reaction (Fig. 4) are bis(2-phenylpropyl)phosphine oxide **1**, tris(2-phenylpropyl) phosphine oxide **2**, and potassium(2-phenylpropyl)phosphinite **3**. The conversion was 100 % or 17 % in terms of phosphorus or a-methylstyrene, respectively [40]. When this process was carried out with commercial red phosphorus as the reagent, only tertiary phosphine oxide **2** could be obtained (15 % yield; the phosphorus and α-methylstyrene conversions were 82 % and 18 %, respectively). Thus, PCP is advantageous over "common" red phosphorus for organophosphorus synthesis.

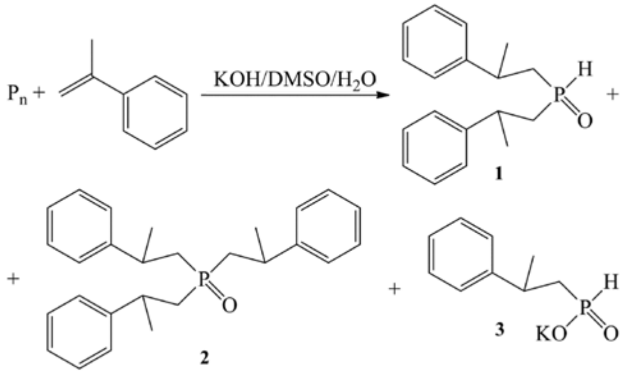


Fig. 4: Reaction scheme of Trofimov-Gusarova reaction between PCP and α-methylstyrene in superbasic medium [40].

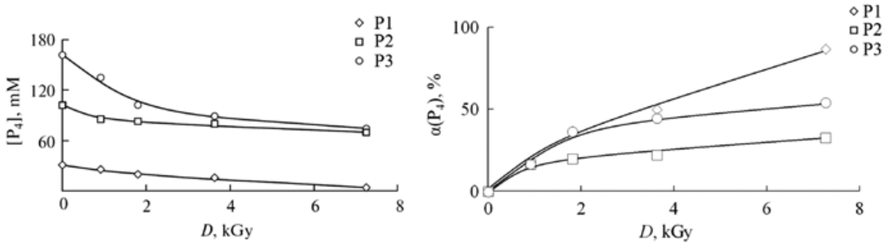


Fig. 5: Kinetic curves for systems P1–P3 with $[BuMeIm]BF_4$. $T = 298$ K, $P = 0.126$ Gy s^{-1}, $[P_4]_0 = 31.0$ (P1), 102.1 (P2), and 160.9 (P3) M.

PCPs were also synthesized in reaction media consisting of only two substances – benzene and IL. The following ILs were used: $[BuMeIm]BF_4$, $[Bu_3OcP]BF_4$, and$[Bu_3OcP]N(SO_2CF_3)_2$ [44].

Phosphorus-containing polymers PCP1, PCP2, and PCP3, synthesized in the presence of $[BuMeIm]BF_4$), $[Bu_3OcP]BF_4$), and $[Bu_3OcP]N(SO_2CF_3)_2$), respectively, were studied. PCP1 and PCP2 are orange, whereas PCP3 is red-orange.

The elemental composition of all the synthesized PCPs was similar – P: 42–52; C: 6–10; H: 2–7; O: 34–49 wt.%. The oxygen originates from contact of the PCPs with air. Enrichment of the surface layers with carbon (20–30 wt.%), fluorine (1 wt.%, PCP1), or nitrogen (9 wt.%, PCP3) was also detected.

The kinetics of the polymerization of elemental phosphorus were studied for the systems with different initial phosphorus concentrations: systems P1–P3, containing $[BuMeIm]BF_4$, systems P4–P6, containing $[Bu_3OcP]BF_4$, and systems P7–P9, containing $[Bu_3OcP]N(SO_2CF_3)_2$. The respective systems were irradiated with ^{60}Co γ-radiation (dose rate $P = 0.237$ or 0.126 Gy s^{-1} using a ferrous sulfate dosimetry system [20]) at 298 K.

Comparison of the kinetics curves of the tetrafluoroborate anion-containing systems P1–P6 (Fig. 5) shows that high conversion of elemental phosphorus was achieved with an intermediate initial concentration of white phosphorus, whereas with low or high initial concentrations, the conversion was low. For systems P4–P9 with phosphonium ILs, an induction period was required for all initial concentrations of elemental phosphorus studied.

The following mechanistic scheme is suggested for formation of the $[P_4 \cdot IL]$ complexes [45]:

$$\text{solv}\,(C_6H_6) - {\wedge\wedge}\rightarrow C_6H_6^{+} + \bar{e} \tag{1}$$

$$\bar{e} \rightarrow \bar{e}_{\text{solv}} \ \text{(solvated electron)} \tag{2}$$

$$C_6H_6^{+} + \bar{e}_{\text{solv}} \rightarrow C_6H_6^{*} \tag{3}$$

$$C_6H_6^{*} \rightarrow C_6H_5^{\bullet} + H^{\bullet} \tag{4}$$

$$P_4 + IL \rightarrow (P_4 \cdot IL) \tag{5}$$

$$P_4 + R^{\bullet} \rightarrow RP_4^{\bullet} \rightarrow \text{polymer} \tag{6}$$

$$(P_4 \cdot IL) + R^{\bullet} \rightarrow \text{polymer} \tag{7}$$

$$R(P_4)_n^{\bullet} + \text{solv} \rightarrow R(P_4)_nR' + R^{\bullet} \tag{8}$$

$$(R(P_4)_nIL)^{\bullet} + \text{solv} \rightarrow R\,(P_4)_nILR' + R^{\bullet} \tag{9}$$

$$2R(P_4)_n^{\bullet} \rightarrow \text{polymer} \tag{10}$$

$$2(\mathrm{R}(\mathrm{P}_4)_n\mathrm{IL})^{\bullet} \rightarrow \text{polymer} \tag{11}$$

$$2\mathrm{R}^{\bullet} \rightarrow \mathrm{R}-\mathrm{R} \tag{12}$$

The overall-rate equation describing the reaction scheme is as follows:

$$-d[\mathrm{P}_4]/dt = k_{\mathrm{eff}}[\mathrm{P}_4]^2 \tag{13}$$

Linearization of the kinetic curves in the $(1/[\mathrm{P}_4])$–t coordinates indicated that the reaction is second order with respect to white phosphorus.

Among the systems under investigation (with both imidazolium and phosphonium ILs), the effective rate constants, k_{eff}, of the radiation-chemical polymerization of elemental phosphorus (Table 3) calculated from the experimental data were higher for the systems with low initial concentrations of elemental phosphorus, $[\mathrm{P}_4]_0$.

As mentioned earlier [45], at low IL concentration, the effective rate constant of the process depends on the IL concentration due to the mobile equilibrium $\mathrm{P}_4 + \mathrm{IL} \leftrightarrow [\mathrm{P}_4 \cdot \mathrm{IL}]$. The data in Table 3 demonstrate that the effective rate constant depends also on the $[\mathrm{P}_4]_0/[\mathrm{IL}]_0$ ratio. Presumably, this is the result of the ability of ILs to structure solutions through intermolecular interactions [46]. The interactions leading to structural organization and the effect on the process were considered under the topochemical contracting sphere model:

$$\ln(1-(1-\alpha)^{1/3}) = \ln k_{\mathrm{T}} + n \cdot \ln t, \tag{14}$$

where α is the conversion, k_{T} is the topochemical reaction constant, n is the kinetic parameter, and t is the reaction time (Table 3). The complicated dependence of the topochemical reaction constant on the $[\mathrm{P}_4]_0/[\mathrm{IL}]_0$ ratio highlights the considerable effect of the IL as a structuring agent on the polymerization of elemental phosphorus.

Notably, the correlation coefficients for systems P7–P9 with the bis(trifluoromethylsulfonyl)imide anion were lower ($R = 0.81$–0.93) than those of systems P1–P6 with tetrafluoroborate anions (0.94–0.99). The SEM data illustrate that systems P7–P9 with the bis(trifluoromethylsulfonyl)imide anion can form planar networks in solution, whereas systems P1–P6 with the tetrafluoroborate anion are more likely to form spherical and ellipsoid micellar structures. Thus, bis(trifluoromethylsulfonyl)imide-containing systems P7–P9 conform less to the topochemical contracting sphere model than the tetrafluoroborate-containing systems P1–P6.

Table 3: Characteristics of radiation-chemical polymerization of elemental phosphorus.

System		$[\mathrm{P}_4]_0$, mM	$[\mathrm{P}_4]_0$/[IL]0	k_{eff}, L/mol s	$\ln k_{\mathrm{T}}$	D, kGy	$\alpha_{\max}$	R
P1	$\mathrm{P_4{-}C_6H_6{-}[BuMeIm]BF_4}$	31	1.2	$1.1 \cdot 10^{-3}$	−10.9	3.4	0.87	0.99
P2		102	4.1	$7.1 \cdot 10^{-5}$	−5.9	0.9	0.33	0.94
P3		161	6.4	$1.8 \cdot 10^{-4}$	−8.2	0.9	0.54	0.97
P4	$\mathrm{P_4{-}C_6H_6{-}[Bu_3OcP]BF_4}$	37	1.5	$1.0 \cdot 10^{-3}$	−14.9	1.8	0.66	0.99
P5		95	3.8	$3.8 \cdot 10^{-5}$	−25.6	3.6	0.14	0.99
P6		158	6.3	$4.9 \cdot 10^{-5}$	−14.9	3.6	0.43	0.96
P7	$\mathrm{P_4{-}C_6H_6{-}[Bu_3OcP]N(SO_2CF_3)_2}$	36	1.4	$1.3 \cdot 10^{-3}$	−8.4	3.6	0.71	0.97
P8		99	4.0	$2.0 \cdot 10^{-4}$	−15.6	1.8	0.50	0.93
P9		158	6.3	$1.8 \cdot 10^{-4}$	−13.2	1.7	0.46	0.81

k_{eff} is the effective polymerization rate constant, $\ln k_{\mathrm{T}}$ is the logarithm of the topochemical reaction constant, D is the absorbed dose for achieving maximal conversion ($\alpha_{\max}$), and R is the correlation coefficient. $T = 298$ K, $P = 0.126$ Gy s^{-1}, $[\mathrm{IL}]_0 = 0.025$ M.

Based on the known dependence of the reaction on the concentration of an amphiphilic compound for monomers with double bonds [47, 48], it could be assumed that the complicated dependence of the topochemical reaction constant on the $[P_4]_0/[IL]_0$ ratio is the result of two competing processes, i.e. formation of $[IL \cdot P_4]$ complexes at low phosphorus concentrations and formation of micellar structures with an increased content of elemental phosphorus at high phosphorus concentrations.

Thus, the process of radiation-chemical polymerization of elemental phosphorus could be tailored to meet the needs of experimenters by the addition of different ILs due to the high sensitivity of the reaction to the characteristics of the medium, its composition, and physicochemical properties.

The shape of the PCP particles could be controlled by changing the type of anion in the IL. The tetrafluoroborate anion promoted the formation of spherical and ellipsoidal particles, whereas the bis(trifluoromethylsulfonyl)imide anion led to formation of scaly particles. In both cases, the synthesized PCPs were amorphous with a layered structure, and the structure of the polymers contained fragments of the reaction medium.

The type of IL and the ratio of the initial concentration of elemental phosphorus to the IL significantly impacted the effective rate constant of the radiation-chemical polymerization of elemental phosphorus. Formation of the PCPs followed second order kinetics with respect to elemental phosphorus, and the optimal absorbed dose for the synthesis was in the 1.7–3.6 kGy range.

Ionic liquids in the radiation-chemical transformation of elemental sulfur

Elemental sulfur is one of the main by-products of oil and gas refining. Currently, there is a worldwide overproduction of sulfur [49]. Annually, about 70 million tons are produced worldwide, including 7.3 million tons in Russia, as a by-product of petroleum refineries and natural gas processing plants [50]. Therefore, the processes of sulfur transformation under ionizing radiation in the presence of ILs was evaluated to determine the possibility of synthesis of other inorganic polymer–polymeric sulfur or sulfur-containing polymers, similar to previously synthesized and investigated PCPs [14, 19, 39, 46]. Polymeric sulfur can be used in industry for vulcanization of rubber and as a plasticizer in concrete or ceramics due to its high resistance to aggressive media, high impact strength, absence of thermal shrinkage strain in composites, insolubility in rubber, etc.

A number of systems comprising elemental sulfur in benzene and in benzene–IL or benzene–DMSO–IL mixtures with various initial concentrations of elemental sulfur were studied (Table 4).

Table 4: Characteristics of radiation-chemical transformation of elemental sulfur at various initial elemental sulfur concentrations.

System		$[S_8]_0$, mM	α_{max}	*D*, kGy	Reaction order	k_{eff}, s^{-1} (I), l/mol s (II)	R
S1	S_8–C_6H_6	96	0.88	3.4	I	$1.1 \cdot 10^{-4}$	0.99
S2	S_8–C_6H_6–$[BuMe_2Im]BF_4$	107	0.68	0.9	II	$1.2 \cdot 10^{-3}$	0.85
S3	S_8–C_6H_6–$[BuMeIm]BF_4$	196	0.89	0.9	II	$5.5 \cdot 10^{-4}$	0.99
S4	S_8–C_6H_6–$[BuMeIm]CF_3SO_3$	203	0.83	1.8	II	$3.3 \cdot 10^{-4}$	0.98
S5	S_8–C_6H_6–$[Bu_3MeP]N(SO_2CF_3)_2$	99	0.73	3.6	II	$7.3 \cdot 10^{-4}$	0.99
S6	S_8–C_6H_6–$[Bu_3DdP]N(SO_2CF_3)_2$	136	0.78	3.6	II	$5.2 \cdot 10^{-4}$	0.96
S7	S_8–C_6H_6–$[Et_3OcP]N(SO_2CF_3)_2$	160	0.81	3.6	II	$5.4 \cdot 10^{-4}$	0.99
S8	S_8–C_6H_6–$[Et_3DdP]N(SO_2CF_3)_2$	215	0.80	1.8	II	$5.4 \cdot 10^{-4}$	0.95
S9	S_8–C_6H_6–$[Bu_3OcP]BF_4$	62	0.68	1.7	II	$2.6 \cdot 10^{-3}$	0.94
S10	S_8–C_6H_6–$[Bu_3DdP]BF_4$	115	0.73	3.4	II	$1.0 \cdot 10^{-3}$	0.99
S11	S_8–C_6H_6–DMSO–$[Bu_3OcP]BF_4$	150	0.97	3.4	I	$2.2 \cdot 10^{-4}$	0.98

k_{eff} is the effective rate constant, *D* is the absorbed dose achieved at maximal conversion (α_{max}), and *R* is the correlation coefficient. $T = 298$ K, $P = 0.126$ Gy s^{-1}, $[IL]_0 = 0.025$ M.

$[BuMeIm]CF_3SO_3$, $[BuMeIm]BF_4$, $[BuMe_2Im]BF_4$, $[Et_3OcP]N(SO_2CF_3)_2$, $[Et_3DdP]N(SO_2CF_3)_2$, $[Bu_3MeP]N(SO_2CF_3)_2$, $[Bu_3OcP]N(SO_2CF_3)_2$, $[Bu_3DdP]N(SO_2CF_3)_2$, $[Bu_3OcP]BF_4$, and $[Bu_3DdP]BF_4$ ILs were employed.

Similar to the phosphorus-containing systems, these systems were irradiated with ^{60}Co γ-radiation (dose rate $P = 0.237$ or 0.126 Gy s^{-1} using a ferrous sulfate dosimetry system [20]) at 298 K. The kinetic data were obtained by titrimetric methods. Based on the blank experiments, the presence of the IL in the system does not affect the determination of elemental sulfur.

For most of these systems, the conversion of elemental sulfur reached 0.7–0.9 at absorbed doses of 2–4 kGy, whereas for systems S2–S4 and S8, this value was reached at about 1 kGy. Notably, in the beginning of the process, the content of elemental sulfur in the systems decreased rapidly. After absorption of the radiation, the concentration and conversion of elemental sulfur reached a plateau (Table 4; Fig. 6).

For systems S2–S4 with imidazolium ILs $[BuMe_2Im]BF_4$, $[BuMeIm]BF_4$, and $[BuMeIm]CF_3SO_3$, which are structurally similar, the physiochemical analysis showed that increasing the number of alkyl radicals in the cation of the IL decreased the solvency of the system. At the same time, system S4 with the imidazolium IL containing the trifluoromethanesulfonate required an induction period, and the maximal conversion, α_{max}, was twice as high as that in systems S2 and S3 with the tetrafluoroborate anions. Together, these observations demonstrate that the effect of the anionic part of the IL on the kinetic parameters for transformation of elemental sulfur outweighs that on the physicochemical characteristics of the system.

For systems S5–S10 with phosphonium ILs, the following results were obtained: with increasing length of the alkyl radical, the solvency of the system for elemental sulfur increased. The systems with tetrafluoroborate anions (S9 and S10) had lower elemental sulfur conversions and lower α_{max} values (about 2–4 times) than those with bis(trifluoromethylsulfonyl)imide anions (S5–S8). Systems S5 and S6 containing 3-*n*-butylalkylphosphonium ILs with long alkyl chains required induction periods.

Thus, both parts of the ILs, the cation as well as the anion, affect the solvency of the system. However, the effect of varying the cation of the IL is more pronounced than that of varying the anion. Presumably, with the former, formation of micelle-like structures between the IL cation and the S_8 molecule is promoted, where the S_8 molecule is a nucleophile possessing lone pairs of electrons, and these structures can stabilize S_8-rich fluctuations.

In common, the systems with imidazolium ILs exhibit higher elemental sulfur conversion than the systems with phosphonium ILs (0.83–0.89 and 0.68–0.81, respectively). To explain this fact, the rate constant for the reaction of the solvated electron with the phosphonium and imidazolium cations (1.6×10^{10} and 3.8×10^{9} l mol^{-1} · s^{-1}, respectively) must be taken into account [36]. Thus, phosphonium ILs are more effective for the removal of primary active particles (solvated electron) from the reaction media. Thiophenols were detected in the reaction products (as an intense black coloration in the lead sulfide test; in system S11 with DMSO, the coloration was much weaker, indicating that the concentration of thiophenols was lower), along with residual elemental sulfur and a resinous brownish deposit (after evaporation of the solution), which is

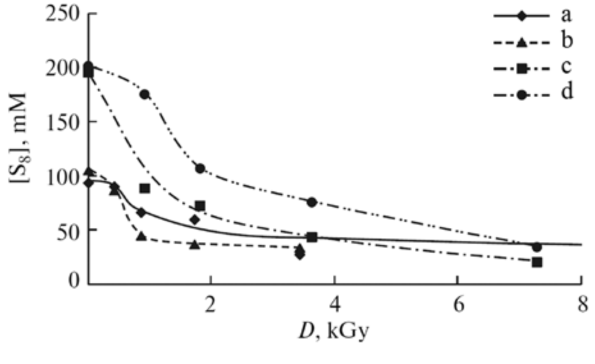


Fig. 6: Elemental sulfur concentration $[S_8]$ versus absorbed dose D in (a) benzene and solutions of (b) benzene–$[BuMe_2Im]BF_4$, (c) benzene–$[BuMeIm]BF_4$, and (d) benzene–$[BuMeIm]CF_3SO_3$ at 298 K and $P = $ (a, b) 0.237 and (c, d) 0.126 Gy s^{-1}.

likely to be oligomeric sulfur-containing products. Elemental sulfur radiolysis under ionizing radiation gave consistent results [51].

Based on the benzene radiolysis data [52] and the experimental data, the following mechanism was proposed for the radiation-chemical transformation of elemental sulfur in a non-aqueous solvent:

$$C_6H_6 -\wedge\wedge\rightarrow C_6H_6^{+} + \bar{e}, \tag{15}$$

$$\bar{e} \rightarrow \bar{e}_{\text{solv}} \text{(solvated electron)}, \tag{16}$$

$$C_6H_6^{+} + \bar{e}_{\text{solv}} \rightarrow C_6H_6^{*}, \tag{17}$$

$$C_6H_6^{*} \rightarrow C_6H_5^{\bullet} + H^{\bullet}, \tag{18}$$

$$C_6H_5^{\bullet} + S_8 \rightarrow C_6H_5-S_8^{\bullet} \rightarrow C_6H_5S_x^{\bullet} + S_y, \tag{19}$$

$$H^{\bullet} + S_8 \rightarrow HS_8^{\bullet} \rightarrow HS_x^{\bullet} + S_y. \tag{20}$$

The formed fragment of the sulfur molecule S_y (cycle of $y < 8$ atoms or a linear diradical), due to its instability, continues to break up into smaller radical fragments, which, as S_8, can participate in various processes, in particular, with the thiophenyl radical:

$$C_6H_5S^{\bullet} + S_y \rightarrow C_6H_5(S_{y+1})^{\bullet}, \tag{21}$$

$$C_6H_5S^{\bullet} + S_8 \rightarrow C_6H_5S-S_8^{\bullet}, \tag{22}$$

$$C_6H_5S^{\bullet} + H^{\bullet} \rightarrow C_6H_5SH, \tag{23}$$

$$2C_6H_5S^{\bullet} \rightarrow C_6H_5S-SC_6H_5, \tag{24}$$

$$SH^{\bullet} + H^{\bullet} \rightarrow H_2S, \tag{25}$$

$$\left.\begin{array}{r} C_6H_5S_x^{\bullet} + S_y \\ 2\ C_6H_5S_x^{\bullet} \\ 2\ S_y: \end{array}\right\} \rightarrow \text{products (including oligomers).} \tag{26}$$

The inclusion of the organic fragments into the structure of the sulfur-containing products can stabilize the compound and also increase the solubility of the oligomers. Thus, the products of the reaction can further participate in radiation-chemical processes. Finally, the rate of the radiation-chemical transformation of elemental sulfur in the presence of ILs is much higher than that without the ILs, and the transformation is primarily accompanied by the formation of thiophenols.

Returning to the synthesis of phosphorus-containing polymers, recall that the polarity of the reaction medium influences the conversion of elemental phosphorus to phosphorus-containing polymers under the action of ionizing radiation in the presence of ILs [53]. Evaluation of system S11 containing 5 mol% DMSO showed that an increase in the polarity of the reaction medium leads to the absence of thiophenols in the final product and to an increase in the sulfur conversion (to 0.97 as compared with 0.68 for the similar system S9 without DMSO). The absence of the thiophenols may be attributed to oxidation of the thiols to disulfides by DMSO. High sulfur conversion was achieved, as the primary products (short-lived DMSO radical cation $(CH_3)_2S^+=O$ and $\bar{e}$) of DMSO radiolysis act as initiating agents in the reactions.

The kinetic orders of the processes involved in radiation-chemical transformation of elemental sulfur were determined by linearizing the kinetic curves. For systems I and XI, these curves were linearized in the coordinates $(\ln[S_8])-t$, and for systems S2–S10, in the coordinates $(1/[S_8])-t$, corresponding to first and second order reactions, respectively, with respect to elemental sulfur (Table 4). Based on these linearizations, the effective rate constants were also determined.

Considering these data, it can be concluded that the steric factor has a strong effect on the rate of the process. The compact tetrafluoroborate anion (compared to the trifluoromethanesulfonate and bis(trifluoromethylsulfonyl)imide anions) induces a faster reaction. At the same time, the increase in the alkyl radical chain length in the tetraalkylphosphonium cation leads to a decrease in the effective reaction rate constant.

Thus, investigation of the transformation of elemental sulfur under high-energy radiation in benzene solution in the presence of ILs, which was carried out herein for the first time, showed that the addition of ILs accelerates the transformation of elemental sulfur. At the adsorbed dose of 2–4 kGy, 70–90 % conversion was achieved. The kinetic parameters of the process strongly depend on the structure of the anionic part of the IL, mainly on the steric factor. Due to this dependence, the effective reaction rate constants are higher for the systems with tetrafluoroborate ILs. The $S_8-C_6H_6$ and $S_8-C_6H_6$–DMSO–$[Bu_3OcP]BF_4$ systems are characterized by first order kinetics with respect to elemental sulfur, whereas all $S_8-C_6H_6$–IL systems exhibit second order kinetics with respect to elemental sulfur. The physicochemical characteristics (e.g. solvency) of the system can be changed by varying of the cationic part of the IL. Thus, the characteristics of the system and the kinetics can be controlled by varying the structure of the IL.

Although the transformation of elemental sulfur to sulfur-containing compounds was detected, the main products are sulfur-containing oligomers and thiophenols. No formation of polymeric forms of elemental sulfur with high degrees of polymerization was detected.

Ionic liquids and elemental sulfur under SHF radiation

One possible reason why ionizing radiation does not transform elemental sulfur to polymers, but only to oligomers, could be the high energy of the ionizing radiation. Thus, an alternative method of initiating the transformation of elemental sulfur was sought. As the alternative, super high frequency (SHF), or microwave, radiation was selected, which is widely used in green chemistry.

The specific features of polymerization under SHF irradiation and the possibility of using ILs in these processes were discussed previously [54]. In short, the use of SHF radiation in industry started in the second half of the 20th century, and SHF has been used in polymerization since the mid-1980s [55–58]. Currently, SHF radiation is widely used in polymer synthesis, namely in polycondensation [59–63], free and controlled radical polymerization [64, 65], polymerization with ring opening [66], polymerization of vinyl monomers [67–69], polymerization with the opening of caprolactam and caprolactone rings [70], polycondensation for the synthesis of polyesters, polyamides [71–73] and polyimides [74, 75], hardening of epoxy [76, 77] and polyurethane resins [78], and polymerization and depolymerization of thermosetting and thermoplastic polymers [79].

SHF initiation is adequate for liquid, solid, and paste media. However, the reagents that can be used are severely limited as the substances must be polar in order to absorb SHF radiation. SHF irradiation promotes polarization of the molecules, thus speeding the reactions [80]. Nonpolar solvents (CCl_4, alkanes, benzene, etc.) do not absorb SHF radiation; thus, in such solutions, the effect of SHF irradiation is directed to the reagents [81]. Elemental sulfur (the reagent of interest in our research) is also nonpolar. To resolve this problem, ILs can be added to the reaction system. Due to the ionic conductivity mechanism, ILs efficiently absorb SHF energy and are quickly heated [82]; therefore, they can be used as solvents and co-solvents (as an addition to nonpolar solvents). In this case, ILs are not only structuring and catalyzing agents, but act primarily as absorption enhancers for media with low absorbing capability [83].

In the present experiment, the main aim was to identify the products of the reaction of elemental sulfur under SHF irradiation. [BuMeIm]PF_6, [Bu_3MeP]$N(SO_2CF_3)_2$, and [Bu_3MeP]$(CH_3)_2PO_4$ were utilized, and the following systems based on these ILs were investigated [84]: a mixture of benzene and [Bu_3MeP]$(CH_3)_2PO_4$, C_6H_6/[Bu_3MeP]$(CH_3)_2PO_4$ (system S12); a solution of sulfur in a benzene–[Bu_3MeP]$(CH_3)_2PO_4$ mixture, $S_8 + C_6H_6$/[Bu_3MeP]$(CH_3)_2PO_4$ (system S13); a solution of sulfur in a benzene–[BuMeIm]PF_6 mixture, $S_8 + C_6H_6$/[BuMeIm]PF_6 (system S14); a solution of sulfur in a benzene–[Bu_3MeP]$N(SO_2CF_3)_2$ mixture, and $S_8 + C_6H_6$/[Bu_3MeP]$N(SO_2CF_3)_2$ (system S5). These systems were heated to 433 K for 180 min with SHF radiation in a Biotage Initiator + microwave reactor (2.45 GHz) system.

NMR was used to identify the structure of the products: ^{1}H 200.3 MHz, ^{13}C 50.3 MHz, ^{31}P 81.0 MHz (Bruker CXP 200, Mendeleev Shared Facility Center), ^{31}P 121.5 MHz (Bruker Avance 300, Shared Facility Center of the Institute of General and Inorganic Chemistry, RAS), and ^{31}P 161.97 MHz (Bruker AMX 400, Shared Facility Center of the Institute of Organoelement Compounds, RAS). The ^{1}H and ^{13}C chemical shifts were measured relative to the signal of the internal C_6H_6; the ^{31}P chemical shifts were measured relative to the external H_3PO_4 signal.

Notably, benzene, the major component of both systems, acts only as a solvent and is not involved in the chemical interactions. This conclusion was made after comparing the ^{1}H and ^{13}C spectra of systems S12 and S13 before and after SHF radiation. Strong singlets were observed in the spectra, corresponding to the hydrogen and carbon atoms of benzene (^{1}H 7.3 ppm, ^{13}C 127.9 ppm). These signals did not change after SHF heating, indicating that the benzene structure was not affected.

The ^{31}P NMR spectra of systems S12 and S13 (Fig. 7) show that SHF heating of system S13 led to the appearance of a singlet at 51.9 ppm and to a change in the relative intensity of the singlets at 35.0 and 5.6 ppm corresponding to the cation and anion of the IL, whereas there were no changes in the profile of system S12 without sulfur. Thus, under these conditions, the IL can react with elemental sulfur via the phosphorus atoms. This claim was verified by the experiments with systems S5 and S14 having ILs with a phosphorus-containing anion and cation, respectively. The ^{31}P NMR spectra of these systems led to the conclusion that the phosphorus-containing anion (hexafluorophosphate anion) reacts with sulfur to a much higher degree than the phosphorus-containing cation (tetraalkylphosphonium). This may be the result of the Lewis basicity of the S_8 molecule due to the lone electron pairs on the sulfur atoms [85], the charge being localized above and below the sulfur ring [86].

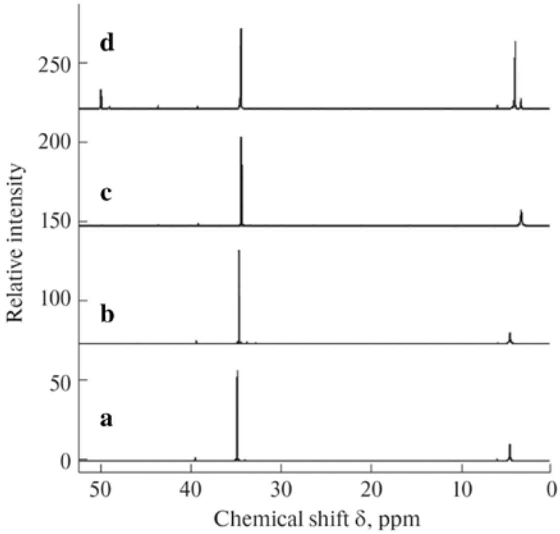


Fig. 7: ^{31}P NMR (121.5 MHz) spectra of (a) system S12 (C_6H_6/[Bu_3MeP]$(CH_3)_2PO_4$) without SHF heating; (b) system S12 (C_6H_6/[Bu_3MeP]$(CH_3)_2PO_4$) after SHF heating at 433 K for 180 min; (c) system S13 ($S_8 + C_6H_6$/[Bu_3MeP]$(CH_3)_2PO_4$) without SHF heating; (d) system S13 ($S_8 + C_6H_6$/[Bu_3MeP]$(CH_3)_2PO_4$) after SHF heating at 433 K for 180 min.

In order to clarify the foregoing claim, the systems with and without sulfur in the mixture of benzene and the following ILs were studied: [BuMeIm] CF_3SO_3, [BuMeIm]PF_6, [BuMeIm]BF_4, [Bu_3OcP]$N(SO_2CF_3)_2$, [Bu_3DdP] $N(SO_2CF_3)_2$, [Bu_3MeP]$N(SO_2CF_3)_2$, [Et_3OcP]$N(SO_2CF_3)_2$, [Et_3DdP]$N(SO_2CF_3)_2$, and [Bu_3MeP]$(CH_3)_2PO_4$. The systems containing fluorine were evaluated using ^{19}F NMR, while the systems containing phosphorus were evaluated using ^{31}P NMR (Bruker CXP 200, Mendeleev Shared Facility Center). The NMR spectra again demonstrated no perceptible changes in the chemical shifts before and after SHF irradiation for the systems with and without sulfur, except for the solution of elemental sulfur in the mixture of benzene and [Bu_3MeP]$(CH_3)_2PO_4$. In this system, a new ^{31}P signal at 51.6 ppm was detected, corresponding to the product of the chemical reaction between the IL and elemental sulfur. Presumably, this is a specific feature of the dimethylphosphate anion, which should be considered in the design of new routes for chemical synthesis.

Thus, it could be concluded that even under mild conditions, ILs can react with substances of relatively low chemical reactivity (e.g. elemental sulfur), although traditionally ILs are considered to be chemically inert green solvents.

Conclusions

From evaluation of radiation-chemical transformation of elemental phosphorus in the presence of ILs, it is hypothesized that fluctuations in the transformation occur with an increase in the concentration of phosphorus due to the solvation effect of the ILs. Phosphorus-containing polymers with fragments of the reaction medium were synthesized, the structure and properties of which depend on the IL added to the system. It was demonstrated that the reaction parameters (e.g. kinetic order of the reaction and effective reaction rate constant) also depend on the IL, thus indicating the possibility of tailoring the process by "tuning" the properties of the IL.

The transformation of elemental sulfur in the presence of ILs under the influence of ionizing and SHF radiation was evaluated for the first time. Despite the general principles of polymerization of inorganic substances, unlike the case of phosphorus, the application of SHF radiation to sulfur in the presence of ILs leads to the formation of sulfur-containing oligomers with a low degree of polymerization, rather than polymers. In this case, it should also be noted that the kinetic parameters of the process significantly depend on the IL.

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