Role of reaction media in "green" radiation-induced polymerization of white phosphorus*

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Abstract: Phosphorus-containing polymers were synthesized using a "green" radiation-induced reaction at room temperature in the presence of ionic liquids (ILs). The nature of ILs allowed us to adjust the properties of reaction media (dimethyl sulfoxide, DMSO–benzene solvents). The effects of various factors on the efficiency of the synthesis of phosphorus-containing polymers are discussed.

Keywords: elemental phosphorus; imidazolium; ionic liquids; phosphonium; phosphorus-containing polymers; radiation-induced polymerization.

INTRODUCTION

Currently available technologies for the synthesis of phosphorus-containing polymers with various dopants have a considerable anthropogenic impact on the environment. We studied the radiation-induced synthesis of phosphorus-containing polymers in the presence of ionic liquids (ILs) to develop a process that meets the principles of green chemistry [1]. The use of ILs allowed us to obtain the product in a high yield with a high selectivity in the absence of intermediate transformations (principle nos. 2, 8, and 9). ILs are not only low-toxicity solvents but also co-reagents (principle nos. 4 and 5). The radiation-initiated process occurs at room temperature and atmospheric pressure (principle no. 6). Furthermore, solvents stable under irradiation can be reused after the separation of the phosphorus-containing polymers (principle no. 7).

Earlier, we studied the radiation-induced polymerization of white phosphorus in the presence of imidazolium ILs [2] and characterized the structure and properties of the resulting phosphorus-containing polymers by means of physicochemical analysis. We found that the structure and concentration of the IL considerably affected the rate of polymerization and calculated kinetic characteristics (reaction rates and apparent rate constants) of radiation-induced polymerization of elemental phosphorus in the presence of ILs in a dimethyl sulfoxide (DMSO)–benzene mixed solvent.

Taking into consideration the fact that the variety of ILs allows us to carry out fine "tuning" of the reaction system for the purpose of "management" of radiation-chemical processes, the purpose of this research was to track the influence of the structure and the nature of ILs on the efficiency of polymerization of white phosphorus.

EXPERIMENTAL

In this study, the following imidazolium ILs (99.9 % purity; Merck, Germany) were used: 1-butyl-3-methylimidazolium trifluoromethanesulfonate $[BMIm]^+[CF_3SO_3]^-$, 1-butyl-3-methylimidazolium tetrafluoroborate $[BMIm]^+[BF_4]^-$, 1-butyl-3-methylimidazolium hexafluorophosphate $[BMIm]^+[PF_6]^-$, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[EMIm]^+[N(SO_2CF_3)_2]^-$, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[BMPyr]^+[N(SO_2CF_3)_2]^-$, 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate $[HMIm]^+[(C_2F_5)_3PF_3]^-$.

The following phosphonium ILs (99.9 % purity; Nippon Chemical, Japan) were used: triethyl-octylphosphonium bis(trifluoromethylsulfonyl)imide $[EOP]^+[N(SO_2CF_3)_2]^-$, triethyldodecyl phosphonium bis(trifluoromethylsulfonyl)imide $[EDP]^+[N(SO_2CF_3)_2]^-$, tri-*n*-butylmethylphosphonium bis(trifluoromethylsulfonyl) imide $[BMP]^+[N(SO_2CF_3)_2]^-$, tri-*n*-butyloctylphosphonium bis(trifluoromethylsulfonyl)imide $[BOP]^+[N(SO_2CF_3)_2]^-$, tri-*n*-butyldodecylphosphonium bis(trifluoromethylsulfonyl)imide $[BDP]^+[N(SO_2CF_3)_2]^-$, tri-*n*-butyloctylphosphonium tetrafluoroborate $[BOP]^+[BF_4]^-$, tri-*n*-butyldodecylphosphonium tetrafluoroborate $[BDP]^+[BF_4]^-$, tri-*n*-butyl methyl phosphonium dimethylphosphate $[BMP]^+[PO_2(OCH_3)_2]^-$.

White phosphorus was purified in accordance with a modified procedure [3]. The solvents (benzene and DMSO) were purified using the standard procedures [4].

The polymerization of white phosphorus was performed in ampoules in an inert atmosphere. The ampoules with solutions were irradiated with ^{60}Co γ-radiation (dose rate $D^{•}$ = 0.59 Gy/s). The polymerization temperature T was 298 K. After irradiation, the ampoules were opened and the precipitate was filtered off. The residual concentration of phosphorus in the solution was determined by titrimetry (with an alcohol–benzene solution of iodine taken in an excess) [3,5]. The absorbed dose D was calculated using the ferrous sulfate dosimetric system [6].

The reaction products were characterized by elemental analysis, IR spectroscopy (Bruker Tensor 27M instrument), and X-ray diffraction analysis (DRON-3M diffractometer). The micrographs were taken using Tesla BS 340 scanning electron microscope.

Apparent reaction rate constants (K) of white phosphorus polymerization were calculated from the kinetic data on the residual concentration of the elemental phosphorus in the reaction mixture after the irradiation

RESULTS AND DISCUSSION

According to elemental analysis data, the samples of phosphorus-containing products formed under the irradiation of white phosphorus solutions in DMSO–benzene with the addition of ILs (Fig. 1) had the following composition, wt %: P, 67–70; C, 6–7; H, 1.8–2; and O, <20. The IR spectra of all of the phosphorus-containing samples exhibited absorption bands corresponding to P–O–H (1460 cm^{-1}), P–O (1380 cm^{-1}), P–H (1150 and 970 cm^{-1}), and P–C (720 cm^{-1}) bonds: thus, the organic fragments of the solvent were linked to phosphorus. A weak absorption band at 500 cm^{-1} can be attributed to P–P vibrations. All of these absorption bands were also typical of the phosphorus-containing polymers prepared earlier by the γ-initiated polymerization of white phosphorus in benzene [7].

It should be mentioned that Allen et al. [8] considered the relative radiation stability of 1,3-di-alkylimidazolium cation-based ILs. They appear to be relatively radiation-resistant, and there is certainly no major decomposition of the organic component.
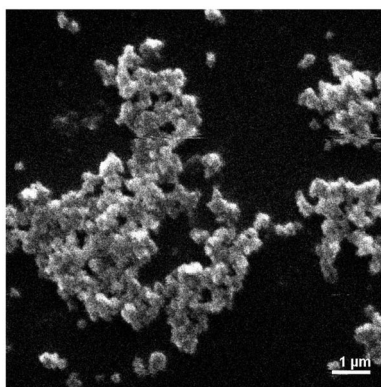
Fig. 1 Micrograph of the phosphorus-containing polymer produced by the irradiation of a solution of white phosphorus in DMSO–benzene with the addition of an IL. $T = 298$ K, $D^{\bullet} = 0.59$ Gy/s, $D = 24.7$ kGy, $[P_4]_0 = 0.013$ M, $[[BMPyr]^+[N(SO_2CF_3)_2]^-]_0 = 0.16$ M.

The analysis of kinetic data demonstrated that the nature of the IL strongly affected the rate and energetic efficiency (radiation-chemical yield) of the radiation-chemical process (Table 1).

Table 1 Radiation-chemical yields G (P_4 molecule/100 eV) of phosphorus-containing polymers in the presence of ILs in DMSO–benzene (50 wt %) solution ($T = 298$ K, $D^{\bullet} = 0.59$ Gy/s).

Ionic liquid	$[BMIm]^+$ $[CF_3SO_3]^-$	$[BMIm]^+$ $[BF_4]^-$	$[BMIm]^+$ $[PF_6]^-$	$[EMIm]^+$ $[N(SO_2 CF_3)_2]^-$	$[BMPyr]^+$ $[N(SO_2 CF_3)_2]^-$	$[HMIm]^+$ $[(C_2F_5)_3PF_3]^-$	Without IL
$[P_4]_0$, M	0.044	0.065	0.044	0.040	0.025	0.031	0.040
$[IL]_0/[P_4]_0$	13.33	13.89	14.49	4.65	12.35	7.46	–
G	455 ± 46	47 ± 5	69 ± 7	60 ± 6	31 ± 3	32 ± 3	8 ± 1

Indeed, the radiation-chemical yield changed by one to two orders of magnitude upon the addition of ILs to the system.

Such a behavior of the reaction systems can result from the following:

(1)   the formation of IL-P_4 complexes;
(2)   the structurization of white phosphorus solutions in the presence of ILs;
(3)   the increased role of ion–radical processes in the radiation-induced polymerization of white phosphorus.

As far as (1) is concerned, the structure of aromatic solvents allows them to participate in the formation of the systems with weak interactions. This conclusion is consistent with our earlier results [9], in particular, the data on ^{31}P NMR spectra, and the quantum-chemical calculations of the P_4–C_6H_6 system [10,11].

Earlier, we found that the highest reaction rates in the radiation-induced polymerization of elemental phosphorus were observed in the DMSO–benzene (50–85 wt %) solvent. One might expect that, in a system containing an inorganic monomer (white phosphorus) and an amphiphilic compound such as an IL (which dissociates into ions and has an affinity to both polar and nonpolar components of the reaction medium), the structurization (2) and the formation of nanoscale aggregates can occur, as was observed in similar systems [12–15].

Chang et al. [16] studied the models of electrolyte solutions in the presence of ILs and predicted the occurrence of structural changes at concentrations of ILs around 0.02 M and at temperatures close

to 314 K. As could be seen from the data in Table 2, in our case the IR spectra of the test ILs and their solutions in the benzene–DMSO–P_4 system exhibited absorption bands due to the formation of hydrogen bonds between the hydrogen of aromatic ring and the oxygen of DMSO.

Table 2 Typical IR absorption bands (in the range of 3800–3000 cm^{-1}) of pure ILs and their shift in benzene–DMSO–P_4 system due to the H-bonds formation with DMSO.

Ionic liquid	Pure IL, ν, cm^{-1}	IL in solution, ν, cm^{-1}
$[BMIm]^+[CF_3SO_3]^-$	3550	3440
$[BMIm]^+[BF_4]^-$	3650	3450
$[BMIm]^+[PF_6]^-$	3700	3440
$[BMPyr]^+[N(SO_2CF_3)_2]^-$	3700	3450
$[HMIm]^+[(C_2F_5)_3PF_3]^-$	3720	3460

Based on the polarity of ILs [12], one could anticipate the formation of nanoscale agglomerates in nonpolar media (in our situation, in benzene). For example, Hanke et al. [17] investigated some aspects of the interaction of ILs with aromatic compounds. The dissolubility of benzene in the ILs was used as the test characteristic. By the molecular simulation of the dynamics of benzene solution in dimethylimidazolium hexafluorophosphate, it was found that the difference between the chemical potentials of pure benzene and its solution in the IL depends on the solvent and is higher than 4 k_BT. This value is sufficient for explaining the observed solubility difference. Hanke et al. [17] related the observed phenomena to variations in the local structure of a medium around benzene in the presence of ILs.

Holbrey et al. [18] suggested the formation of IL–benzene liquid clathrates in 1,3-dimethylimidazolium hexafluorophosphate–benzene (2:1) solutions, where benzene molecules are surrounded by anion–cation cages with the strong interactions between the cation methyl groups and the benzene π-system.

In systems with higher content of benzene molecules (1:1), Lachwa et al. [19] observed the formation of a tube-like structure with a rectangular cross-section around the IL cations.

As one moves from the 2:1 to the 1:1 type of inclusion compound, the observed trend suggests how cage-like structures of liquid clathrates can assemble at higher proportions of benzene (e.g., 1:1.5 or 1:2 of IL:benzene ratio). That is, from the perspective of the structure of the benzene molecules, the IL and aromatic system evolves from unidimensional stacks, to tube-like orientations, and, finally, to cage-like arrangements.

In [20] it was found that in [BMIm][PF_6]–naphthalene mixtures ($T = 350$ K) the residual ionic fraction forms nanometric droplets, whereas the neutral ion pairs condense into molecular-thin chains that stretch between ionic droplets and sometimes fold into blobs also of nanometric dimension.

Ion aggregation, discussed in [20] in the case of [BMIm][PF_6], is expected to play an important role also for applications involving ILs and their mixtures with organic solvents of low dielectric constant. On the one hand, the transition marks the stability boundary of the IL phase and might limit the composition range that can be considered for specific applications. On the other hand, the transition provides a further handle to monitor and to change the properties of IL samples. In this respect, the relative sharpness of the transition represents an additional advantage that might allow a precise control of the system state and behavior.

Such agglomerates are capable of trapping and solvating quasi-free electrons formed in the reaction mixture under the irradiation, thus affecting (3). Some evidence in favor of this assumption is given below.

For 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium tetra-fluoroborate, and 1-butyl-3-methylimidazolium hexafluorophosphate (possessing the same cation), the maximum value of the apparent rate constant shifted toward higher IL concentrations in the anion order $[BF_4]^- \rightarrow [PF_6]^- \rightarrow [CF_3SO_3]^-$ in the range of $[IL]_0/[P_4]_0$ ratios of 0–45 (Fig. 2). The greatest change in the apparent rate constant was observed in the case of $[BMIm]^+[CF_3SO_3]^-$ (IL I). The dependence of apparent rate constants on the $[IL]_0/[P_4]_0$ ratio for ILs with different cations (Fig. 3) suggests the participation of the cationic moiety of an IL in the reaction.
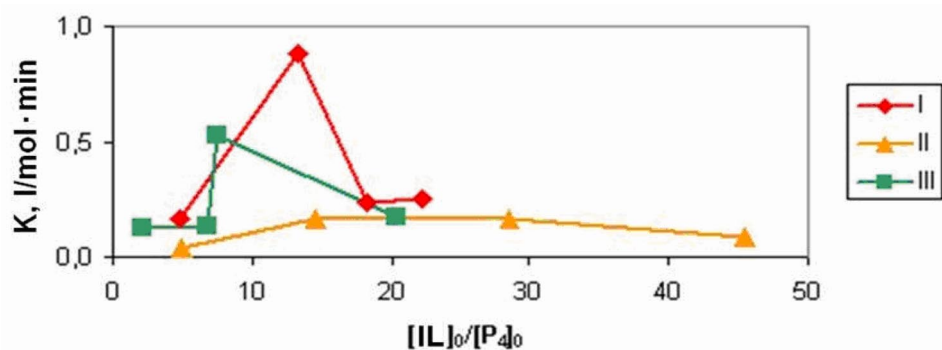

Fig. 2 Dependence of the apparent reaction rate constant of white phosphorus polymerization (*K*) on the ratio between the reagents (T = 298 K, $D^\bullet$ = 0.59 Gy/s): (I) $[BMIm]^+[CF_3SO_3]^-$, (II) $[BMIm]^+[BF_4]^-$, and (III) $[BMIm]^+[PF_6]^-$.
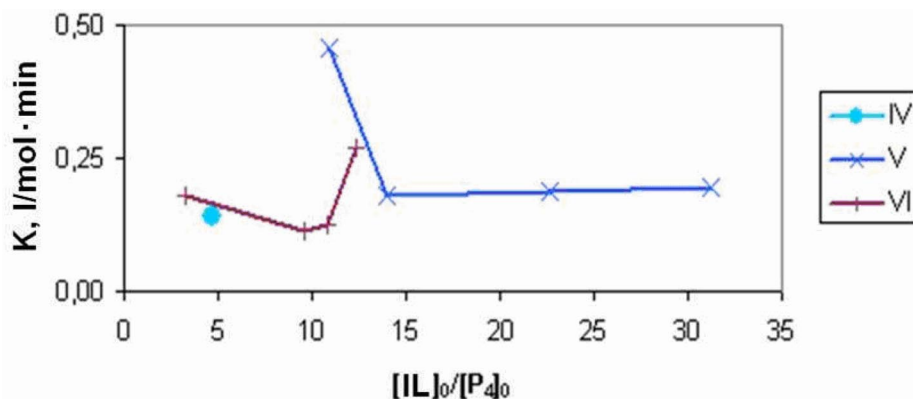

Fig. 3 Dependence of the apparent reaction rate constant of white phosphorus polymerization (*K*) on the ratio between the reagents (T = 298 K, $D^\bullet$ = 0.59 Gy/s): (IV) $[EMIm]^+[CF_3SO_3]^-$, (V) $[BMPyr]^+[N(SO_2CF_3)_2]^-$, and (VI) $[HMIm]^+[(C_2F_5)_3PF_3]^-$.

Previously [21], we found that the tetraphosphorus molecule behaved like an olefin molecule in polymerization reactions. It is likely that the reaction kinetics observed in phosphorus solutions in the presence of ILs is similar to the kinetics of polymerization of various olefins.

The influence of the IL cation on the olefin polymerization process has been discussed in [22], where 1-*n*-alkyl-3-methylimidazolium hexafluorophosphate was used as a reference compound. It was found that the efficiency of olefin oligomerization was almost independent of the type of the cation.

We found that, as opposed to the imidazolium ILs, the radiation-induced formation of phosphorus-containing polymers in the presence of the phosphonium ILs did not occur in DMSO–benzene (but

occurred in propan-2-ol–benzene). Evidently, this was due to the reactivity of the intermediates formed during the radiolysis of the reaction system components. As can be seen in Table 3, phosphonium ions are capable of actively trapping solvated electrons, thus prohibiting the polymerization reaction of white phosphorus.

Table 3 Rate constants of the reaction of organic compounds with water radiolysis products at $T = 298$ K [23].

Compound (ion)	Solvated electron	Hydrogen atom	Hydroxyl radical
Tetraphenyl-phosphonium ion	$(1.6 \pm 0.3) \times 10^{10}$	$(1.5 \pm 0.3) \times 10^9$	$(3.0 \pm 0.3) \times 10^9$
Pyrrolidonium ion	$(7.5 \pm 1.5) \times 10^6$	–	5.7×10^9
Imidazolium ion	$(3.8 \pm 0.5) \times 10^9$	–	–
Benzene	$(1.2 \pm 0.2) \times 10^7$	$(9.0 \pm 2.0) \times 10^8$	$(5.2 \pm 1.5) \times 10^9$

The observed complicated dependence of the apparent rate constant of polymerization of white phosphorus on the concentration and nature of the IL can be due to a number of phenomena.

Under the action of ionizing radiation, there is no difference in the set of primary products of radiolysis formed both in the reaction media containing ILs and free of them (the relative concentration and, consequently, the electronic fraction of an IL in the system was no higher than 0.1; thus, the direct action of ionizing radiation on the IL can be ignored). With consideration for this fact, the observed phenomena can be related to the structural characteristics of the IL and to a structural reorganization in the solution.

The appearance of IL in the reaction mixture leads not only to an increase of the reaction rate, but also to a change in the kinetic order of the reaction on white phosphorus from the first [7] to the second [2]. Such a phenomenon can be concerned both with the formation of structures with participation of IL–P_4 and with the special features of the interaction of reagents with the initiating intermediates formed in the process of the radiolysis.

In the case of the irradiation of ILs in the solution, the reaction of solvated electrons with molecules of IL is the most effective one (see Table 3) [24]. One might suppose that the products of this reaction initiate transformations of the white phosphorus into phosphorus-containing polymers. In this case, the change of the apparent reaction rate constant (**K**) will reflect the changes in the reaction system. If we consider solvated electron to be a co-reagent in the reaction, the collision cross-section of the reaction would be defined by the cross-sectional area of the IL molecule or the IL–P_4 complex.

In this case, one could use Lewis–Trautz equation

$$k = p \cdot \pi(r_A + r_B)^2 [8k_B T/(\pi m^*)]^{0.5} e^{-E/k_B T}$$

where p is the steric factor; r_A is the radius of the IL–P_4 complex, and r_B is the radius of the solvated electron (cut-off value); $\pi(r_A + r_B)^2 \approx \pi(r_{IL\text{-}P4})^2$ is the collision cross-section of the IL–P_4 complex; $m^* = (m_A \cdot m_B)/(m_A + m_B)$ is the reduced mass; E is the activation energy; k_B is the Boltzmann constant; and T is the temperature, K.

Unfortunately, we have no data on the $r_{IL\text{-}P4}$ value, so we used the molar volume of the IL (V), assuming that $V^{2/3}$ is in the first approximation proportional to the collision cross-section (S) of the IL–P_4 complex.

If we assume, that the reaction of the solvated electron with the IL–P_4 complex is the rate-limiting stage, then **K** and k would demonstrate a symbate change (equation, see above). Table 4 summarizes the values of apparent rate constants (**K**) and cross-sectional areas (S) of particles.

Table 4 Apparent rate constants (K) and cross-sectional areas (S) for imidazolium ILs.

No.	Ionic liquid	Molar weight M, g/mol	Density ρ, g/cm^3	K, l/(mol·min) for [IL]$_0$/[P$_4$]$_0$ = 10	$S \sim kV^{2/3}$, nm^2
II	[BMIm]$^+$[BF$_4$]$^-$	226	1.17	0.12	0.47
III	[BMIm]$^+$[PF$_6$]$^-$	284	1.38	0.45	0.49
I	[BMIm]$^+$[CF$_3$SO$_3$]$^-$	289	1.29	0.63	0.52
V	[BMPyr]$^+$[N(SO$_2$CF$_3$)$_2$]$^-$	422	1.43	0.50	0.62
VI	[HMIm]$^+$[(C$_2$F$_5$)$_3$PF$_3$]$^-$	612	1.56	0.12	0.75

It can be seen (Table 4) that the apparent rate constant increased with the increase of the cross-sectional areas of ILs (I)–(III) with identical cations (i.e., with the size of the anion). We assume that the ability of IL molecules to trap active intermediates or to cause structural changes in the reaction medium can be responsible for the observed behavior.

CONCLUSION

The analysis of both published data and our experimental results allowed us to formulate the hypothesis of the occurrence of fluctuations of the concentration of white phosphorus in the benzene–DMSO–IL–P$_4$ system due to solvation interactions in this system.

Such a control of chemical reactions by the "tuning" of the reaction medium is an important area in the development of green chemical technology.

ACKNOWLEDGMENTS

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