CHEMICAL PROBLEMS OF THE DEVELOPMENT OF NEW MATERIALS AND TECHNOLOGIES
Minsk 2003

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LEWIS ACID COMPLEXES: SYNTHESIS AND APPLICATION IN POLYMERIZATION PROCESSES

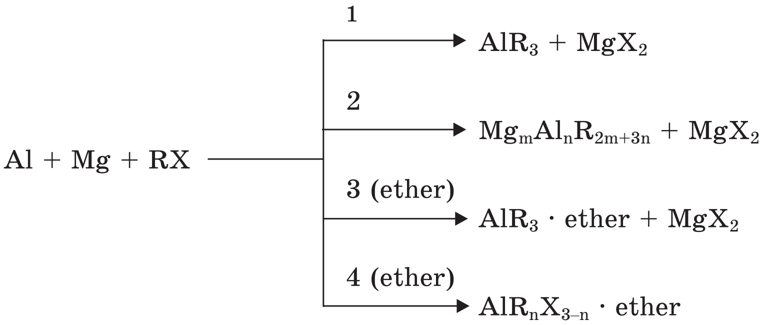
INTRODUCTION

Organoaluminium compounds (OAC) are characterized by various types of reactivity, catalytic activity, and a wide spectrum of synthetic applications. Their high reactivity towards oxygen and water creates numerous difficulties in handling them and limits considerably their use, especially in polymerization processes. Using OAC complexes with electron donor compounds (etherates) removes the above named difficulties because these complexes are more stable while manifesting high activity in many reactions, and displaying specific properties in a number of cases [1–4].

Systematic work performed in the area of synthesis and investigation of properties of OAC and their complexes have made it possible to develop simple and convenient synthetic methods for the named compounds, along with studying their physicochemical properties and catalytic activity in polymerization processes [1–10].

Mechanistic studies performed on the reaction of aluminium, magnesium and alkyl halides in paraffine hydrocarbon medium, both in the presence of an ether and without it, have shown that this complex heterogeneous process occurs via intermediate formation of dialkylmagnesium compounds, their complexes with alkylaluminium species, as well as alkylmagnesium and alkylaluminium halides [11]. The overall process mechanism depends on not only the electron transfer from the metal surface to alkyl halide but on subsequent alkylation reactions of alkylaluminum halides as well, which proceed easier with higher alkyl halides due to better hydrocarbon solubility of higher alkylmagnesium compounds [12]. The data obtained offered the possibility of targeted syntheses of AlR_3 [2, 11–14], of the respective etherates [11, 12, 15, 16] and of $Mg_mAl_nR_{2m+3n}$ [3, 12, 17, 18] to be performed according to the following scheme 1.

Many etherates of OAC and their derivatives were obtained by direct reactions between the components [1, 4]. It is noteworthy that, in a number of cases, these apparently simple reactions are complicated by disproportionation processes, radical exchange, etc. For separation of alkylaluminium halide mixtures, a method has been developed based on formation of solid alkylaluminium dihalide complexes with 1,4-dioxane, 2,2’-dipyridyl, 1(2)-alkyltetrazoles or 2,5-disubstituted tetrazoles [1, 4, 19].



1 – R = n-C_5H_{11} – n-$C_{10}H_{21}$;
2 – R = n-C_4H_9 – n-$C_{10}H_{21}$, n/m = 0.5–30 ;
3 – R = C_2H_5 – n-$C_{10}H_{21}$;
4 – R = i-C_3H_7, i-C_4H_9, cyclic-C_6H_{11}.

Scheme 1. Synthesis of aluminium alkyls, aluminium alkyls etherates and magnesium aluminium alkyls

Studies of physicochemical properties of OAC and their complexes made it possible to forecast the behavior of these compounds in their most important application area – as catalysts in polymerization and co-polymerization of α-olefines, dienes, and other monomers [1–9, 20–45].

AOC complexes with dialkylmagnesium compounds, in combination with $TiCl_4$, possess high catalytic activity in styrene and ethylene polymerization and also in copolymerization of ethylene with higher α-olefins [6, 26, 28, 30, 31, 33]. The mentioned catalytic systems have been found to be effective in the synthesis in super high molecular weight isotactic polystyrene [6]. We have recently shown [46, 47] that the catalytic system on the basis of the complexes of higher OAC with dialkylmagnesium compounds promotes the obtaining of high molecular weight poly(1-hexene) with considerable percentage of isotactic polymer. Alkylaluminium halides and their etherates are efficient complex forming species in alternating copolymerization of styrene or pentadiene-1,3 with methylmetacrylate or acrylonitrile [35–38]. Complexes of chlorine-containing aluminium compounds with diphenyl ether are highly active catalysts of cationic preparation procedures of liquid rubbers [8, 42, 43, 48, 49], polymeric petroleum resins (PPRs) and petroleum polymerizate (PP), used for production of paintwork materials and in construction sector [50–57].

Investigations of trans-pentadiene-1,3 oligomerization under the action of isobutylaluminium dichloride etherate have shown that these processes possess features characteristic of «living» polymerization [24]. The interest towards the «living» and controlled polymerization is due primarily to the possibility of obtaining polymers with a well-defined structure, molecular weight, molecular weight distribution (MWD) and functionality, or block copolymers with pre-determined length and block sequence, without admixture of homopolymers. During the last years, we made considerable efforts in studying the «living» polymerization of styrene, aimed at the search for new initiating systems suitable for industrial use to perform controlled cationic polymerization of industrial C_9 fraction of liquid products of gasoline pyrolysis.

1. THE «LIVING» CATIONIC POLYMERIZATION OF STYRENE

1.1. Polymerization in the system 1-chloro-1-phenylethane/$TiCl_4$/Bu_2O

In this paper, the results of studies of styrene polymerization in the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O at -15 °C are presented. It is known that tertiary alkyl and aryl halides in combination with $TiCl_4$ and in the presence of strong electron donors (ED) ($[TiCl_4] >> [ED]$) are often used for initiation of the «living» cationic polymerization of styrene at low temperatures (– 80 °C). The initiator we have chosen belongs also to this compound class but is characterized by greater stability under usual conditions. Introduction of a weak ED in excess with respect to the Lewis acid (LA) into the system studied has been shown to promote the controlled polymerization [58]. For realization of the «living» cationic polymerization of styrene, dibutyl ether (Bu_2O) has proved to be the most suitable system component; therefore, the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O was studied in more detail.

Controlled polymerization in the named system was found to proceed in media of low polarity (mixture of 1,2-dichloroethane (DCE) with hexane). With all this going on, a decrease in solvent polarity leads to a substantial narrowing in molecular weight distribution of the polymer obtained: from $M_w/M_n = 2.14$ to ~ 1.75 at DCE : hexane = 2:1 and DCE : hexane = 1:1, respectively [59]. Investigation of styrene polymerization at various Bu_2O concentrations has shown that the optimal $[TiCl_4] : [Bu_2O]$ ratio was 1:2. Further increase in the ether content led to a conventional (non-controlled) polymerization, as evidenced by a decrease in M_n with increasing monomer conversion, whereas MWD retained its quite narrow value ($M_w/M_n = 1.88$) [60].

The results obtained allowed optimal conditions and reagent ratios to be found and the «living» polymerization of styrene to be performed in the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O. Thus, M_n of the polymer increases with increasing monomer conversion, the straight line of the «M_n-conversion» relationship passes through the origin, and the experimental data correlate well with those calculated (solid line in Fig. 1). This evidences the absence of a chain transfer reaction in the system. It is noteworthy, that MWDs for the polymers synthesized ($M_w/M_n = 1.46 – 1.56$) are more narrow as compared with those for other polystyrenes obtained in other systems based on $TiCl_4$.

The second relationship shown in Fig. 1 (dotted line) indicates that the chain growth is a first order reaction with respect to the monomer, i.e. the concentration of active species remains constant in the course of reaction. This is evidence of the absence of an irreversible chain termination.

The data presented above are evidence of «living» character of styrene polymerization under the conditions studied. Earlier we have found that the lifetime of active species is longer than the time of complete conversion of the monomer [59]. This fact is an indication of a prevailing role of chain growth processes over those of irreversible chain termination.

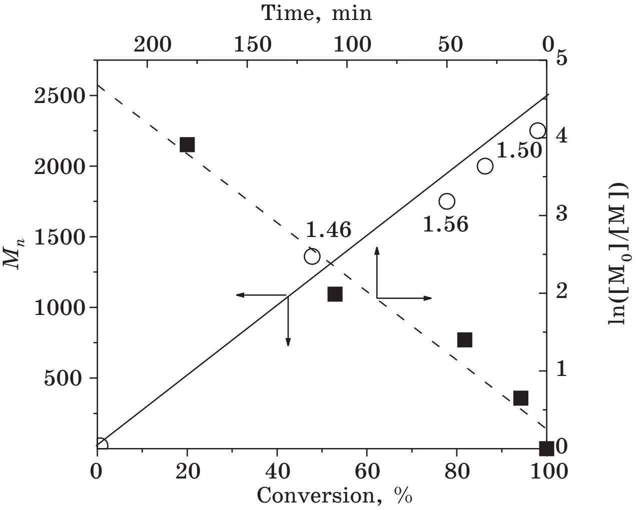


Fig. 1. Molecular weights as function of monomer conversion, and ln($[M]_0$/[M]) versus time in the polymerization of styrene with 1-phenylethyl chloride/$TiCl_4$/Bu_2O/ –15 °C; $[M]_0$ 0.82 M; $[I]_0$ $3.5 \cdot 10^{-2}$ M; [$TiCl_4$] 0.14 M; [Bu_2O] 0.28. Numbers are MWD values. The straight line corresponds to theoretically calculated M_n values

^{1}H NMR spectroscopy data indicate the presence of only chlorine terminal groups in the macromolecules. The number-average molecular weight (M_n = 1760) calculated from the ^{1}H NMR spectrum is virtually the same as the M_n value measured using gel permeation chromatography (GPC) (M_n = 1720), and is quite close to that determined from the relationship [M_0]/[I]·104, where [M_0] and [I] are concentrations of the monomer and the initiator (M_n = 1600) [60].

The first-order (with respect to the monomer) relationship for styrene polymerization in the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O at various $TiCl_4$ concentrations is shown in Fig. 2. The values for apparent rate constants (k_{papp}) determined from the slopes of straight line plots of ln([M_0]/[M]) vs. polymerization time were $1.1 \cdot 10^{-2}$, $2.1 \cdot 10^{-2}$ and $3.9 \cdot 10^{-2}$ min^{-1}, for $TiCl_4$ concentrations of 0.07, 0.14 and 0.21 M, respectively [61].

As is seen from Fig. 3, the reaction order with respect to $TiCl_4$ for styrene polymerization in the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O is 1.09, that is very close to 1. Taking into account that the first order in isobutylene polymerization is observed when [initiator] ≥ [$TiCl_4$] [62], we have suggested that initiation of polymerization in the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O is performed by means of a small amount of $TiCl_4$ resulting from dissociation of its complex with Bu_2O. In this case, the instantaneous concentration of $TiCl_4$ < [initiator] and, according to [62], the reaction order with respect to $TiCl_4$ should be equal to 1. On the other hand, the free ether formed as a result of dissociation of the complex can interact with the growing species by solvation. This leads to both decrease in the overall polymerization rate and suppression of side reactions. The suggested reaction mechanism is presented in the scheme 2 [61].

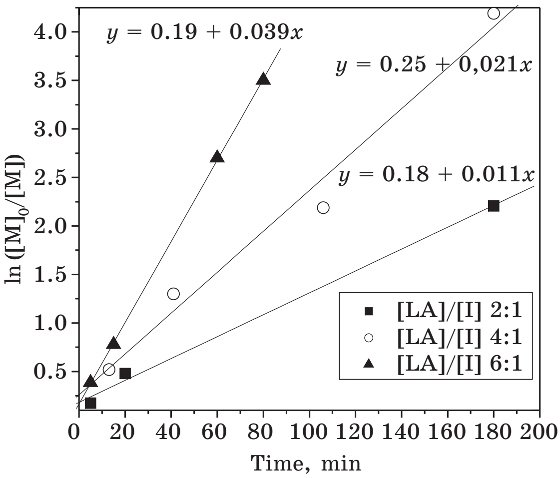


Fig. 2. The plot of ln($[M_0]/[M]$) vs. polymerization time in the system 1-phenylethyl chloride/$TiCl_4/Bu_2O$ at –15 °C using various $TiCl_4$ concentrations; $[M_0] = 0.82$ M; $[I] = 3.5 \cdot 10^{-2}$ M; $[TiCl_4] = 2\ [Bu_2O]$

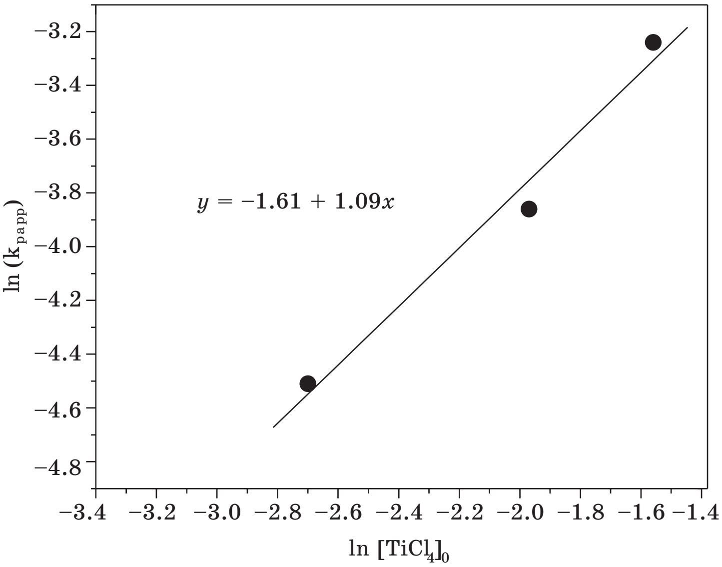
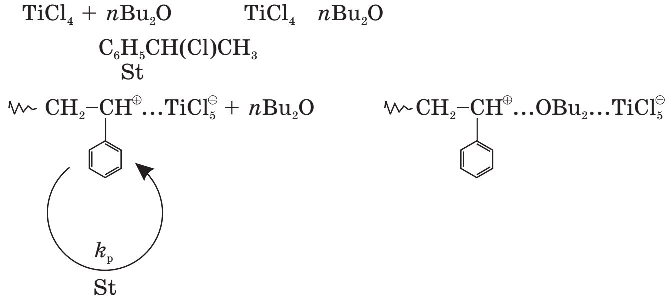


Fig. 3. Reaction order of $[TiCl_4]$ for styrene polymerization with 1-phenylethyl chloride/$TiCl_4/Bu_2O$/ –15 °C; $[M]_0$ 0.82 M; $[I]_0$ $3.5 \cdot 10^{-2}$ M; $[TiCl_4]=2[Bu_2O]$



Scheme 2. Styrene polymerization mechanism in the system 1-phenylethyl chloride/$TiCl_4$/Bu_2O

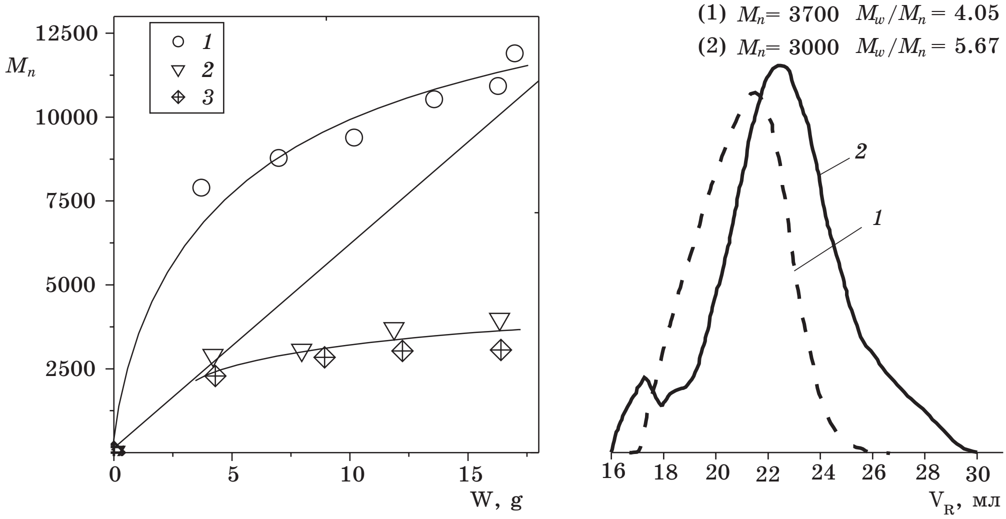
In that way, the studies performed made it possible to avoid low temperatures used to obtain «living» polymerization of styrene in systems based on $TiCl_4$, and to develop initiator systems with a potential of industrial use.

1.2. Polymerization in systems based on $AlCl_3$ etherates

It is known that aluminium trichloride is quite widely used in industrial practice as a co-initiator in cationic polymerization of styrene and other monomers. However, it is characterized by a rather low selectivity with respect to the chain growth reaction, and causes a number of side reactions to proceed. For the time being, there are no reports in the literature about realization of the «living» polymerization of styrene in the presence of aluminium trichloride.

At the same time, preliminary studies have revealed that when styrene polymerization is performed in the systems $H_2O/AlCl_3 \cdot O(C_6H_5)_2$ [63] and $H_2O/AlCl_3 \cdot O(C_4H_9)_2$, [64], no irreversible chain termination is seen, and M_n of the polymer increases with increasing its yield. However, lower M_n value as compared to that calculated indicates that a chain transfer reaction is involved in the named systems. A more detailed study of the system based on $AlCl_3 \cdot O(C_4H_9)_2$ has shown that, depending on polymerization conditions, the experimental M_n values for the polymer either exceed the calculated values (which is evidence of a slow or incomplete initiation) or are lower than the latter, which points to a chain transfer reaction present in the system (Fig. 4*a*) [65].

It is important to note that a polymer with a more narrow MWD is formed in styrene polymerization in the system $H_2O/AlCl_3 \cdot O(C_4H_9)_2$ than in the 1-phenylethyl chloride/$AlCl_3 \cdot OBu_2$ (Fig. 4b). The molecular weight distribution curve is unimodal in the case of styrene polymerization in the system $H_2O/AlCl_3 \cdot OBu_2$, i.e. the process takes place involving only one type of active species – ion pairs. At the same time, a small peak in the area of high molecular weights (at low V_R values) observed in the polymerization using the 1-phenylethyl chloride/$AlCl_3 \cdot OBu_2$ system is an indication of participation of free ions, along with ion pairs, in the chain propagation process.



a *b*

Fig. 4. Molecular weights as function of polymer yield in the polymerization of styrene with $AlCl_3 \cdot OBu_2$ at –15 °C; $[AlCl_3 \cdot OBu_2]$ = 0.03 M; $[H_2O]$ = 0.023 M (1, 2); [1-phenylethyl chloride] = 0.023 M (3). The straight line corresponds to theoretically calculated M_n values (a). GPC traces of polystyrene obtained by the $H_2O/AlCl_3 \cdot OBu_2$ (1) and 1-phenylethyl chloride/$AlCl_3 \cdot OBu_2$ (2) (b)

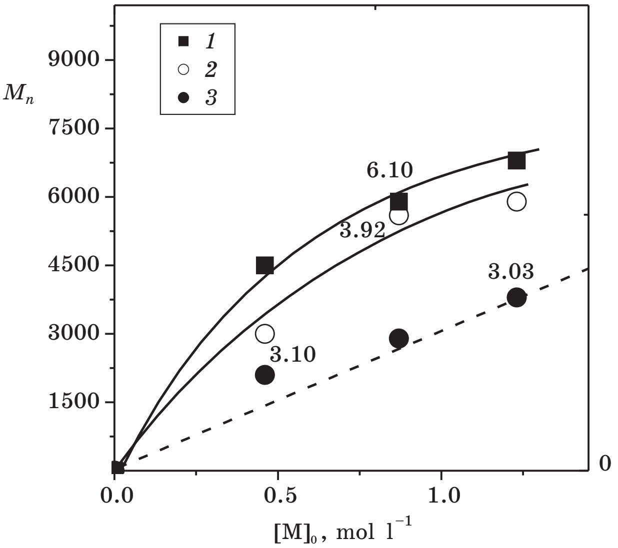


Fig. 5. Molecular weights as function of monomer concentration in the polymerization of styrene in the presence of $AlCl_3 \cdot OBu_2$: $[AlCl_3 \cdot OBu_2]$ 0.05 M, [I] 0.04 M; [I]= 1-phenylethyl chloride (1), 1-phenylethanol (2), 2-phenyl-2-propanol (3). T= –15 °C. The dotted line corresponds to theoretically calculated M_n values

Within the framework of these studies, the effects of initiator structure on molecular weight distribution characteristics of polymers obtained in the presence of $AlCl_3 \cdot OBu_2$ were investigated. It has been found that initiators containing donor groups (–OH) promoted the controlled polymerization of styrene and led to polymers with a more narrow MWDs (Fig. 5). In the system 2-hydroxy-2-phenylpropane/$AlCl_3 \cdot OBu_2$, a «living» polymerization of styrene takes place: molecular weight of the polymer increases with the monomer concentration, and a good correlation of experimental data with the respective calculated values is observed. The polymer MWD decreases with increasing conversion of the monomer (Fig. 5) [66, 67].

In our opinion, the controlled polymerization of styrene in the system 2-hydroxy-2-phenylpropane/$AlCl_3 \cdot OBu_2$ is due to the formation *in situ* of a weaker Lewis acid ($AlCl_2OH$). This leads to a shift in the equilibrium between active and «dormant» species towards formation of the latter, as well as to acceleration of exchange reactions between them, which favors the control of M_n and narrowing its MWD. At the same time, the fact that dibutyl ether forms a fairly stable complex with the Lewis acid ($\Delta H \sim -36.5$ kcal/mol) favors a decrease in momentary concentration of the acid, which leads to suppression of side processes involving the latter. On the other hand, the ether may participate in stabilization of growing chains of polymerization by solvating them or forming donor-acceptor compounds.

Thus, the studies we have performed made it possible for the first time to realize a «living» cationic polymerization of styrene in the presence of a common industrial Lewis acid.

2. SYNTHESIS AND MODIFICATION OF PETROLEUM POLYMERIC RESINS

The intense development of petrochemical industry promoted the creation of a new group of synthetic film-forming substances for the manufacture of paintwork materials – the petroleum polymeric resins. The PPRs are also widely used as binding, plasticizing or dispersing additives in various composite materials employed as substitutes for products of natural and synthetic origin, while maintaining, and sometimes improving their physicochemical and performance characteristics. The use of PPRs is promising due to a broad-range and inexpensive raw material source (waste and side products of industrial-scale syntheses of ethylene and propylene, mainly the C_9 fraction). Furthermore, the manufacture of PPRs and their attendant compounds is one of the trends in profound integrated processing of oil stock [54, 55].

Fundamental investigations of the cationic polymerization mechanism of styrene [63–67], which is one of the major monomers of the C_9 fraction, have shown that the most promising method for preparation of PPRs is cationic polymerization. This is mainly due to the fact that the major monomers contained in the C_9 fraction – styrene, vinyltoluenes, dicyclopentadiene, indene, α-methylstyrene – are quantitatively polymerized by cationic mechanism only. Moreover, under certain conditions, the polymer yield may exceed the one theoretically calculated on the basis of monomer content, which may be explained by the inclusion of aromatic solvent molecules into the polymer chain owing to reactions of chain transfer to the solvent [63].

While performing cationic polymerization experiments with the C_9 fraction, donor-acceptor complexes of $AlCl_3$ with dibutyl and diphenyl ethers, ethyl acetate and carbamide were investigated [54]. It has been found that the most suitable catalyst for industrial use is aluminium trichloride diphenyl etherate, which is characterized by a relatively simple preparation procedure and high stability; the cationic polymerization proceeds rapidly in its presence (1–2 h) and the yields are quantitative [55, 68–70].

Properties of PPRs are known to depend directly on composition of the fractions used for synthesis. At the same time, the contents of hydrocarbon components in the industrial fractions are different. They are determined by composition of the starting raw materials and by pyrolysis conditions. So, depending of monomer composition of the fractions, the resulting PPRs may differ in melting points (60-140 °C) and M_n (350-850). The quantity and ratio of monomers in a fraction determines not only the PPR yields but, to a significant extent, their properties as well. On oligomerization of a fraction containing a large quantity of dicyclopentadiene (30 %), resins with low softening temperatures are formed. An increase of styrene content in the fraction leads to increase in T_{soft}. High content of dicyclopentadiene units in the oligomer chains imparts high elasticity and good adhesive properties to the paintwork materials (films) obtained on their basis. In that way, by varying relative contents of these monomers in a fraction, one can obtain various properties of coatings prepared on their basis, in accordance with their intended use [54, 55, 68].

Besides the fraction composition, other parameters of the oligomerization process, such as temperature, catalyst quantity, modifier and deacfivator nature, exert significant influence on properties of the resins obtained. Optimal concentration of the catalytic complex has been found to be 1–1.5 % (w/w) in a fraction. Introduction of small amounts of maleic anhydride (up to 2 % in a fraction) increases adhesive properties and melting point of the PPRs, which contributes to improvement of quality of the PPR-based films [55].

A significant disadvantage of the PPRs obtained by cationic polymerization is their darker colour as compared to resins synthesized by procedures based on the radical mechanism. It has been found that the colour of resins obtained is significantly affected in the stage of catalyst deactivation. The brightest resins were obtained when using ethylene oxide, propylene oxide, or mixtures of acetone or ethyl alcohol with water as deactivators [54]. The regularities in oligomerization reaction found in these experiments allowed wasteless technologies to be developed for synthesis of PPRs and of an analogue of petroleum polymer-based drying oil [68-70].

The wide range of application areas of PPRs is due, first of all, to their availability and the ability to replace many expensive compounds of natural origin. On the other hand, modification of PPRs by imparting to them hydrophilic properties would make it possible to extend significantly their application areas. Sulphonation and maleinization are the most efficient modification methods for hydrocarbon polymers.

We have performed preliminary studies of sulphonation of polystyrene having molecular weight of up to 3000, which is comparable to that of PPRs obtained by cationic polymerization. The obtained results allowed the reaction conditions, solvent and sulphonating agents to be selected for the synthesis of water-soluble polystyrene. Taking into account the fact that PPRs represent a multicomponent system involving various monomer units, the C_9 fraction that contains the largest quantities of styrene-containing monomers has been selected for the study. The nature of sulphonating agent and the starting reagent ratio have been found to affect significantly both the yields of water soluble resins and content of sulpho-groups introduced. For PPRs sulphonation, chlorosulphonic acid, oleum, and sulphur trioxide complexes with dioxane proved to be the most suitable agents. The studies we have performed made it possible to develop optimal sulphonation parameters for PPRs and PP to prepare modified polymers with various degrees of sulphonation [71]. Some of the sulphonated resin samples (sulpho-PPRs) were tested as concrete plasticizers. Preliminary results have shown that concrete sorts of greater density and enhanced homogeneity as compared with unplasticized ones could be obtained using these samples. Moreover, application of sulpho-PPRs as concrete plasticizers allowed the deformation of autogenic shrinkage to be reduced [72].

In that way, the possibility of using sulphonated polymeric resins as concrete plasticizers has been demonstrated. Sulpho-PPRs are also promising agents for obtaining water-dilutable paints on their basis.

CONCLUSION

As a result of systematic studies on synthesis and properties of OAC and their complexes, easy preparative methods of synthesis for a number of compounds have been developed, and their physicochemical properties and catalytic activity in polymerization processes have been studied. The detailed investigation of the properties of the OAC complexes with ethers allowed working out a range of effective initiating system in cationic polymerization using etherates of $AlCl_3$ and $TiCl_4$. New catalytic systems capable of initiating styrene «living» cationic polymerization were established. These systems being suitable for synthesis of polystyrene with controlled molecular weight, as well as molecular weight distribution and quantitative functionality, are perspective to use in industry. The results obtained in these studies allowed targeted synthesis to be performed of PPRs and PP with pre-determined physicochemical and technical indices, which could be used as film-forming agents in paintwork materials and as concrete plasicizers, as well as for obtaining water-dilutable paints.

Based on the catalytic technology for preparation of petroleum polymer resins and petroleum polymerizate developed at the Research Institute for Physical Chemical Problems of the Belarusian State University, a wasteless manufacturing of bright thermostable resins has been created.

REFERENCES

1. *Mardykin V. P., Gaponik P. N., Popov A. F.* // Russian Chemical Reviews. 1979. Vol. 48, № 5. P. 905.
2. *Gaponik L. V., Mardykin V. P.* // Vestn. Belorussk. Univ. Ser. 2. 1988. № 3. P. 3.
3. *Gaponik L. V., Mardykin V. P., Gavrilenko V. V.* // Organomet. Chem. USSR. 1990. Vol. 3, № 2. P. 111.

4. *Kaputsky F. N., Mardykin V. P., Gaponik L. V.* // Chemical problems of development of new materials and technologies. Minsk. 1998. P. 169.
5. *Kaputsky F. N., Mardykin V. P., Pavlovich A. V.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1994. № 1. P. 115.
6. *Gaponik L. V., Antipova A. M., Morozova T. K., Mardykin V. P.* // J. Appl. Polym. Sci. 1989. Vol. 38. P. 1979.
7. *Kaputsky F. N., Mardykin V. P., Gaponik L. V., Zimina T. L.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1996. № 2. P. 110.
8. *Kaputsky F. N., Mardykin V. P.* // Cationic oligomer of 1,3-pentadiene: synthesis, characteristics and application. Minsk. 1997.
9. *Kaputsky F. N., Mardykin V. P., Kostjuk S. V., Gaponik L. V.* Living carbocationic polymerization of styrene and its derivatives. The selected works of the Belarusian State University. Minsk. 2001. Vol. 5. P. 471.
10. *Mardykin V. P., Gaponik L. V.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1999. № 4. P. 55.
11. *Mardykin V. P., Gaponik L. V., Morozova T. K.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1987. № 2. P. 67.
12. *Gaponik L. V., Mardykin V. P., Pavlovich A. V.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1994. № 3. P. 78.
13. *Gaponik L. V., Mardykin V. P., Gaponik P. N.* // USSR P. 706417; Byull. Izobret., 1979. № 48.
14. *Gaponik L. V., Mardykin V. P.* // Izv. Vusov. Khim. I Khim. tehnolog. 1983. Vol. 26, № 1. P. 30.
15. *Gaponik L. V., Mardykin V. P.* // Russian J. Org. Chem. 1977. Vol. 47, № 7. P. 1579.
16. *Gaponik L. V., Mardykin V. P.* // Izv. Vusov. Khim. I Khim. tehnolog. 1979. Vol. 22, № 10. P. 1194.
17. *Gaponik L. V., Mardykin V. P., Gaponik P. N.* // USSR P. 691455; Byull. Izobret., 1979. № 33.
18. *Gaponik L. V., Mardykin V. P.* // Russian J. General Chem. 1985. Vol. 55, № 6. P. 1341.
19. *Gaponik L. V., Lesnyak V. P., Gaponik P. N.* // Horizon of organic and organometallic chemistry. 1999. Moscow. Vol. 2. P. 35.
20. *Mardykin V. P., Pavlovich A. V., Irkhin B. L., Gaponik L. V., Morozova S. G.* // Russian J. General Chem. 1986. Vol. 56, № 10. P. 2311.
21. *Pavlovich A. V., Mardykin V. P., Gaponik L. V.* // Russian J. General Chem. 1992. Vol. 62, № 3. P. 541.
22. *Mardykin V. P., Pavlovich A. V., Gaponik P. N.* // Organomet. Chem. USSR. 1992. Vol. 5, № 4. P. 930.
23. *Mardykin V. P., Pavlovich A. V., Gaponik P. N., Baranov O. M.* // Russian J. General Chem. 1982. Vol. 52, № 11. P. 2620.
24. *Mardykin V. P., Pavlovich A. V., Gaponik P. N., Irkhin B. L.* // Vestn. Belorussk. Univ. Ser. 2. 1986. № 1. P. 69.
25. *Mardykin V. P., Antipova A. M., Gaponik L. V., Listratova G. V.* // Vestn. Belorussk. Univ. Ser. 2. 1978. № 2. P. 14.
26. *Antipova A. M., Gaponik L. V., Sviridov S. V., Mardykin V. P.* // Polym. Sci. Ser. B. 1983. Vol. 25, № 3. P. 170.
27. *Antipin L. M., Shmidel L. E., Larionov O. G.* et al. // Organomet. Chem. USSR. 1990. Vol. 3, № 6. P. 1279.
28. *Mardykin V. P., Antipova A. M., Gaponik L. V.* // Polym. Sci. Ser. B. 1981. Vol. 23, № 1. P. 52.
29. *Antipova A. M., Morozova T. K., Gaponik L. V.* et al. // Vestn. Belorussk. Univ. Ser. 2. 1984. № 2. P. 14.

30. *Antipova A. M., Morozova T. K., Gaponik L. V., Mardykin V. P.* // Polym. Sci. Ser. B. 1986. Vol. 28, № 3. P. 182.
31. *Antipova A. M., Gaponik L. V., Mardykin V. P.* // Complex organometallic catalyst of olefin polymerization. 1980. Chernogolovka. P. 83.
32. *Voronova E. I., Valendo A. J., Gaponik L. V., Mardykin V. P.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1988. № 5. P. 83.
33. *Ivancheva N. I., Severova N. N., Smolyanova O. V.* et al. // DDR P. 243171.
34. *Mardykin V. P., Morozova T. K.* // Izv. Vusov. Khim. I Khim. tehnolog. 1984. Vol. 27, № 3. P. 357.
35. *Mardykin V. P., Morozova T. K., Pritytskaya T. S.* et. al. // Izv. Vusov. Khim. I Khim. tehnolog. 1981. Vol. 24, № 8. P. 1018.
36. *Antipova A. M., Morozova T. K., Kulevskaya I. V., Mardykin V. P.* // Polym. Sci. Ser. B. 1984. Vol. 26, № 3. P. 170.
37. *Martinovich K. B., Gurash G. V., Mardykin V. P., Gaponik L. V.* // Dokl. Natsion. Akad. Navuk Belarusi. 1978. Vol 22, № 7. P. 631.
38. *Mardykin V. P., Gaponik L. V.* // Vestn. Belorussk. Univ. Ser. 2. 1997. № 3. P. 3.
39. *Mardykin V. P., Pritytskaya T. S., Gurash G. V., Pochernayev N. M.* // Vestn. Belorussk. Univ. Ser. 2. 1981. № 1. P. 27.
40. *Mardykin V. P., Pavlovich A. V.* // Vestn. Belorussk. Univ. Ser. 2. 1991. № 3. P. 24.
41. *Mardykin V. P., Antipova A. M., Gurash G. V., Sviridov S. V.* // Russian J. Appl. Chem. 1979. Vol. 52, № 6. P. 1424.
42. *Mardykin V. P., Irkhin B. L., Pavlovich A. V.* et. al. // Russian J. Appl. Chem. 1984. Vol. 57, № 5. P. 1157.
43. *Pavlovich A. V., Mardykin V. P., Antipin L. M., Kusaev A. I.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1992. № 3–4. P. 103.
44. *Gaponik L. V., Zimina T. L., Mardykin V. P.* // XVII All-union conference on chemistry of complexes compound. Moscow. 1996. P. 30.
45. *Mardykin V. P., Morozova T. K., Rakhimov R. X.* et. al. // USSR P. 71579032. 1990.
46. *Kaputsky F. N., Vasilenko I. V., Kostjuk S. V., Gaponik L. V.* // Vestn. Belorussk. Univ. Ser. 2. 2002. № 2. P. 15.
47. *Kostjuk S. V., Vasilenko I. V., Gaponik L. V., Kaputsky F. N.* // Modern trends in organometallic and catalytic chemistry. Moscow. 2003. P. 80.
48. *Mardykin V. P., Morozova S. G., Gaponik L. V., Chuprakova L. D.* // Russian J. Appl. Chem. 1998. Vol. 71. P. 1041.
49. *Mardykin V. P., Raysnoy V. D., Pavlovich A. V.* et. al. // Plastmasy. 1986. № 7. P. 57.
50. *Mardykin V. P., Pavlovich A. V., Gaponik L. V., Kaputsky F. N.* // Russian P. 2057764. 1996.
51. *Kaputsky F. N., Mardykin V. P., Gaponik L. V., Zimina T. L.* // Belarusian P. 2331. Byull. Izobret., 1997. № 3.
52. *Kaputsky F. N., Mardykin V. P., Gaponik L. V., Milchanina T. L.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1998. № 2. P. 91.
53. *Kaputsky F. N., Mardykin V. P., Gaponik L. V., Milchanina T. L.* // Vestn. Belorussk. Univ. Ser. 2. 1998. № 3. P. 11.
54. *Kaputsky F. N., Mardykin V. P., Gaponik L. V., Lesnyak V. P., Kostjuk S. V.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 2000. № 3. P. 48.
55. *Kaputsky F. N., Mardykin V. P., Gaponik L. V., Lesnyak V. P., Kostjuk S. V., Milchanina T. L.* // Russian J. Appl. Chem. 2002. Vol. 75, № 6. P. 1006.
56. *Kaputsky F. N., Mardykin V. P., Gaponik L. V., Lesnyak V. P., Kostjuk S. V.* // Vestn. Belorussk. Univ. Ser. 2. 2000. № 1. P. 3.
57. *Mardykin V. P., Gaponik L. V.* // Vestn. Belorussk. Univ. Ser. 2. 2001. № 1. P. 16.
58. *Kostjuk S. V., Kaputsky F. N., Mardykin V. P., Gaponik L. V.* // Chemistry and physics of polymers in the 21 century. Chernogolovka. 2000. P. 2–64.

59. *Kostjuk S. V., Kaputsky F. N., Mardykin V. P.* et. al // Dokl. Natsion. Akad. Navuk Belarusi. 2002. Vol. 46. P. 74.
60. *Kostjuk S. V., Kaputsky F. N., Mardykin V. P., Gaponik L. V., Antipin L. M.* // Polym. Bull. 2002. Vol. 49. P. 251.
61. *Kostjuk S.V.* // Polym. Bull. 2003. (in press).
62. *Puskas J. E., Lanzendorfer M. G.* // Macromolecules. 1998. Vol. 31. P. 8684.
63. *Kaputsky F. N., Mardykin V. P., Kostjuk S. V., Gaponik L. V.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 1999. № 2. P. 96.
64. *Kostjuk S. V., Mardykin V. P., Gaponik L. V., Kaputsky F. N.* // Vestsi Natsiyan. Akad. Navuk Belarusi. 2000. № 2. P. 47.
65. *Kostjuk S. V., Kaputsky F. N., Mardykin V. P., Gaponik L. V.* Physic and chemistry of polymers: synthesis, properties and application. 2002. Vol. 8. P. 210.
66. *Kostjuk S. V.* Dissertation Ph.D. Institute of Physical Organic Chemistry of the National Academy of Sciences of Belarus. Minsk. 2002. P. 74.
67. *Kostjuk S. V., Mardykin V. P., Gaponik L. V.* et. al. // Polym. Sci. 2003. (in press).
68. *Kaputsky F. N., Mardykin V. P., Gaponik L. V.* // Development of imported- replaced technologies and materials in chemistry industry. Minsk. 1999. P. 142.
69. *Kalishuk D. G., Saevich N. P., Kaputsky F. N.* et. al. // Development of imported- replaced technologies and materials in chemistry industry. Minsk. 1999. P. 144.
70. *Kostjuk S. V., Lesnyak V. P., Gaponik L. V.* et. al. // New technologies of recycling of secondary resources. Minsk. 2001. P. 44.
71. *Lesnyak V. P., Kaputsky F. N., Mardykin V. P.* et. al. // New technologies in chemical industry. Minsk. 2002. P. 67.
72. *Tur V. V., Kaputsky F. N., Ignashova O. E.* // The concrete and ferro-concrete in the third millennium. Rostov-na-Dony. 2002. P. 342.