The synthesis of polyvinyl chloride and its copolymers with the participation of a binuclear iron complex

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SUMMARY

It is shown that a cyclopentadienyl dicarbonyl iron dimer \([\text{CpFe(CO)}_2]_2\) in combination with an organohalogen compound is an effective initiator/regulator of the polymerisation of vinyl chloride at temperatures of 50-70°C. The molecular weight characteristics, composition, and certain physicochemical properties of homo- and copolymers synthesised on the basis of vinyl chloride in the presence of the iron complex were investigated.

INTRODUCTION

Polyvinyl chloride (PVC) occupies one of the leading places among thermoplastic polymers in terms of the volume of worldwide production [1] and is the base for many composite materials. On the basis of PVC and its copolymers, more than 1000 types of material and article are produced, which are used for the most varied purposes and with each year gain new areas of application [2].

In the manufacture of modern materials based on PVC, the polymer, as a rule, is combined with different ingredients fulfilling the role of plasticisers, stabilisers, lubricants, colourants, and so on, which give the articles the necessary user properties [3].

At the same time, purposeful change in the properties of polymers can be carried out at the synthesis stage, as it is the stage of chain growth that is responsible for the formation of the structure of the macromolecules and consequently for the main physicochemical characteristics of polymeric materials based on them. The production of macromolecules with a specified combination of properties and molecular weight characteristics has become a reality and been extremely promising in recent years owing to the intensive development of methodology for the controlled synthesis of homo- and copolymers [4, 5].

One of the most universal and actively developed approaches in recent time to the controlled synthesis of macromolecules has been atom transfer radical polymerisation (ATRP) based on a redox reaction of halogen-containing organic compounds with transition metals complexes [4-6]. The given method is being used successfully to solve complex problems associated with the targeted synthesis of functional macromolecules and possesses a number of advantages over other methods of carrying out similar processes [7, 8]. The main merits of ATRP include the universality of the method (tolerance to solvents and additives), the fairly high rates of the process, the possibility of synthesising block copolymers, and the moderate ranges of working temperatures, approaching industrial temperatures.

Methods of controlled radical polymerisation are used effectively for the synthesis of polymers based on styrene and (meth)acrylates, but are practically not used in the synthesis of polyvinyl chloride [7, 8]. One of the problems preventing full-scale controlled synthesis of PVC is the high constant of chain transfer to the polymer [9, 10]. In this connection it is extremely urgent to find new original catalytic systems and composites based on metal complexes for controlling the radical polymerisation of vinyl chloride and regulating the molecular weight characteristics of PVC during synthesis [11]. The solution of this problem at the present time is of both fundamental and applied importance.
EXPERIMENTAL

The iron complex \([\text{CpFe(CO)}_2]_2\) is a commercial product, and its purification by recrystallisation is carried out from hexane by the procedure described in [12]:

\[
\text{Tetrahydrofuran (THF), isopropyl alcohol (IPA), toluene, and other organic solvents were purified by standard procedures. The physicochemical constants of the solvents corresponded to published data [13]. The vinyl chloride (VC) corresponded to GOST 6-01-23-75. When carbon tetrachloride (CCl\textsubscript{4}) was used as the coinitiator, its freshly prepared solution (0.1 M) in toluene was employed.}
\]

Specimens were prepared in the following way: precise amounts of monomer, initiator, and iron complex were placed in glass ampoules and freed of oxygen by freezing the reaction mixture in liquid nitrogen and evacuating the ampoules to a residual pressure of <1.3 Pa, and then polymerisation was carried out at a strictly determined temperature.

Monitoring of the kinetics of polymerisation was done under isothermal conditions by the gravimetric method. The ampoules were placed in an oven for a strictly determined time. At the end of this period, the ampoules were taken out and frozen in liquid nitrogen to discontinue polymerisation. The obtained polymers were precipitated in IPA. In order to remove unreacted monomer, initiator, and metal complex from the polymer, specimens were reprecipitated twice and dried at reduced pressure to constant weight, and the degree of conversion was calculated by means of the formula:

\[
P = \frac{m_{\text{pol}}}{m_{\text{mon}}} \times 100\%
\]

where \(m_{\text{pol}}\) is the mass of the polymer, and \(m_{\text{mon}}\) is the mass of the monomer.

The molecular weight (MW) and molecular weight distribution (MWD) of the polymers were determined by gel permeation chromatography on a Knauer unit with a linear column with a separation limit of \(2 \times 10^6\) Da (Nucleogel GPCM-10; Phenomenex, USA) or a cascade of two columns (Phenogel, with a pore size of \(10^3-10^5\) Å; Phenomenex). As the detectors, use was made of an RI Detector K-2301 differential refractometer and a K-2501 UV detector. The eluent was THF. For calibration, narrowly disperse standards based on polymethyl methacrylate (PMMA) were used. The chromatographic data were interpreted using the ChomGate program.

RESULTS AND DISCUSSION

Among the metal complexes used for the controlled synthesis of macromolecules (the ATRP method), copper, ruthenium, and iron compounds are most widely used [14-16]. Iron complexes occupy a special place among catalysts of the ATRP process in light of the successful combination of low cost and high efficiency. In particular, cyclopentadienyl derivatives of iron are widely used in processes of polymerisation of methyl methacrylate and styrene, and also certain functional monomers [17-19]. In view of this, it was expedient to investigate features of the homo- and copolymerisation of vinyl chloride with the use of systems based on metal complex \([\text{CpFe(CO)}_2]_2\).

As a result of the conducted investigations, it was established that the binuclear carbonyl complex \([\text{CpFe(CO)}_2]_2\) in combination with the organohalogen derivative carbon tetrachloride (CCl\textsubscript{4}) exhibits high activity in the initiation of the polymerisation of VC in the temperature range 50–70°C. Thus, extensive conversion of the monomer is achieved in 15 h (Figure 1).

As shown in Figure 1, when the metal complex is introduced into the system, the polymerisation of VC proceeds without the autoacceleration that is characteristic of the block synthesis of PVC.

The conducted analysis of the molecular weight characteristics of PVC specimens showed that, with
increase in the monomer conversion, there is a certain increase in the molecular weight of the polymer (Figure 2).

The dependences observed in Figure 2 are characteristic of processes of controlled radical polymerisation [4, 5]. At the same time, the high value of the rate constant of chain transfer during the synthesis of PVC [8] has a great influence on the molecular weight of the obtained polymer and makes it impossible to achieve effective control of the molecular weight (MW) and of the molecular weight distribution (MWD). The synthesised specimens are characterised by a unimodal MWD, but the coefficient of polydispersity has relatively high values ($M_w/M_n \geq 1.9$). This indicates the possibility of the formation of a “dead” polymer, chiefly on account of the chain transfer that is characteristic of VC [9].

In this connection, the molecular weight of industrially produced PVC is controlled most often by changing the polymerisation temperature. With increase in the synthesis temperature, the ratio of the constant of chain transfer to the monomer to the constant of chain growth increases, as the activation energy of chain transfer is higher than the activation energy of chain growth [9, 10]. Therefore, increase in the polymerisation temperature leads to a reduction in the molecular weight of the PVC. Note that the indicated features of the radical polymerisation of VC are observed when the binuclear carbonyl iron derivative [CpFe(CO)$_2$]$_2$ is used in the synthesis of the polymer in the temperature range 50-70°C (Figure 2, curves 1 and 2).

Thus, on the basis of the conducted investigations on the polymerisation of VC in the presence of binary systems based on [CpFe(CO)$_2$]$_2$ and analysis of published data [15, 20], initiation of the process is possible by Scheme 1.

The reversible interaction of the metal complex with the organohalogen compound leads to initiation of polymerisation and makes it possible to carry out fragment-by-fragment growth of the polymer chain in the process of PVC synthesis.

As mentioned above, during the classical radical polymerisation of VC, the MW of the polymer does not change with increasing conversion. However, the use of the proposed systems based on iron complexes makes it possible to conduct successive increase in the molecular weight of the PVC. Furthermore, with the use of the binuclear iron complex [CpFe(CO)$_2$]$_2$, post-polymerisation of VC can be carried out.

In particular, in order to conduct the given process, new portions of monomer and metal complex [CpFe(CO)$_2$]$_2$ are added to PVC separated at 65% conversion, and synthesis of the polymer is carried out at 70°C in butyl acetate as the solvent. Figure 3 gives data on the MWD of the synthesised PVC. As follows from the data presented, the MWD curve of the polymer obtained by post-polymerisation (curve 2) is unimodal in character and is shifted successively into the high-molecular-weight region ($M_n = 7400, M_w/M_n = 2.7$) in relation to the initial macroinitiator (curve 1) ($M_n = 5500, M_w/M_n = 2.8$).

Thus, increase in the MW of the polymer by comparison with the initial specimen indicates the occurrence of post-polymerisation and the subsequent possibility of using a PVC macroinitiator in processes of synthesis of copolymers with monomers of different activity that are based on it.

Figure 2. The dependence of the number-average molecular weight on the conversion of PVC synthesised in the presence of 0.125 mol% [CpFe(CO)$_2$]$_2$ and 0.25 mol% CCl$_4$ at different temperatures: 1 – 70°C; 2 – 50°C

Figure 3. The MWD curves of PVC synthesised in the presence of [CpFe(CO)$_2$]$_2$ (0.125 mol%), T = 70°C: 1 – PVC macroinitiator; 2 – post-PVC (VC conversion 5% within 28 h)

Scheme 1.
The proposed approach makes it possible not only to modify the properties of the synthesised PVC but also to produce polymers consisting of fragments of different nature, i.e., to "link" often incompatible polymers.

For the case of a polymer of vinyl chloride produced in the presence of the complex \([\text{CpFe(CO)}_2\text{]_2}\) and \(\text{CCl}_4\), an investigation was made of its activity as a macroinitiator in the process of synthesising block copolymers with methyl methacrylate (MMA), styrene (ST), and vinyl acetate (VA).

To produce a block copolymer, corresponding monomers were added to the synthesised PVC (macroinitiator), and their polymerisation was observed.

Analysis of the molecular weight characteristics of the synthesised specimens of block copolymers showed that the MWD curves were unimodal. This indicates the homogeneity of the composition of the copolymers formed. Modes of the polymer are successively displaced towards higher MWs in relation to the initial homopolymer (Figures 4a and b), which is due to the addition of the introduced monomer to the PVC macroinitiator, and consequently to growth of the molecular weight of the specimens.

Methods of NMR and IR spectroscopy were used to assess the composition of the synthesised copolymers, and differential scanning calorimetry was used to investigate their thermal behaviour (Table 1). As follows from the data obtained, the introduction into the PVC molecule of units of a second monomer of different nature and activity leads to loss of regularity of the initial macromolecule and has a certain influence on its flexibility, leading to considerable changes in the temperature transitions of the polymer, in particular the glass transition temperature [21].

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It was established that the content of MMA units in the obtained PVC–PMMA specimen amounts to 66%. The introduction of units of methacrylic monomer into the polymer leads to an increase in the value of the glass transition temperature of the synthesised copolymer to \(T_g = 116^\circ C\). This is probably due to reduction in chain flexibility of the initial PVC on account of the units of rigid-chain PMMA entering the copolymer. A VC homopolymer is characterised by a glass transition temperature of \(~80^\circ C\) [9]. At the same time, the presence of ST units in the PVC macromolecule (amounting to 74% in the synthesised PVC-PST copolymer) also limits the mobility of the macromolecules and leads to an increase in the glass transition temperature of the specimen to \(T_g = 104^\circ C\) owing to the presence in the polymer chain of bulky substituents [benzene rings] of PST. Thus, as a result of introducing units of vinyl monomers, there is an increase in the thermal stability of the synthesised polymer based on PVC. At the same time, the introduction into the macroinitiator (PVC) of VA units leads to a reduction in the glass transition temperature of the PVC-PVA copolymer to \(T_g = 43^\circ C\) (the content of VA units in the specimen amounts to 70%). The VA units probably act as an internal plasticiser in this case.

CONCLUSIONS

1. A system based on the binuclear iron complex \([\text{CpFe(CO)}_2\text{]_2}\) and carbon tetrachloride makes it possible to conduct the polymerisation of VC without autoacceleration to extensive conversions in a
temperature range approximating the conditions of industrial PVC synthesis. Here, in the presence of the proposed metal complex systems, there is a slight increase in the molecular weight of the polymer with increasing VC conversion.

2. A vinyl chloride polymer obtained with the participation of the metal complex $\text{[CpFe(CO)$_2$]}_2$ acts as a macroinitiator and can be successfully applied in the synthesis of (co)polymers of VC with monomers of different activity, which makes it possible to modify certain physicochemical properties and characteristics of PVC in the process of synthesis.

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REFERENCES
