Chemical technology of oligomers production from homopolymer based on epichlorohydrin and morpholine

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Abstract. In this paper, the effect of different solvents on the spontaneous polymerization reaction of morpholine and epichlorohydrin is studied. Also, the factors influencing the polymerization reaction have been established: temperature, proportions of initial substances, optimal values of such parameters as temperature. On the basis of the developed technology the yield of oligomeric product with epichlorohydrin based on morpholine 92-95% was determined. The structure of the synthesized oligomeric substance was established by spectral methods, IR, PMR spectroscopy. The technological scheme for the preparation of polymer products based on 3-chloro-1-morpholyl-2-isopropylacrylate was also developed and the influence of reaction time, temperature and ratio of initial substances on the process was studied. Preparation of oligomer based on morpholine with epichlorohydrin. Processes and technology for obtaining homopolymers based on 3-chloro-1-morpholyl-2-isopropylacrylate were developed.

1 Introduction

The versatile application of multifunctional carbonyl nitrogen-containing monomers and the polymeric materials derived from them spans across a myriad of industries, underscoring their significance in modern technologies [1]. These compounds find utility in textile and light industry, contributing to the creation of advanced fabrics and materials. In the realm of medicine, they play a crucial role in the development of medical devices and pharmaceuticals, showcasing their versatility in improving healthcare technologies [2]. The automotive industry benefits from their use in enhancing the performance and durability of various components, while agriculture exploits these compounds for innovations in crop protection and soil management [3].

Moreover, the fragrance and cosmetic industries leverage carbonyl nitrogen-containing monomers for their unique properties, contributing to the creation of perfumes and cosmetic formulations [4]. In the fields of radio engineering and electrical engineering, these compounds find application in the development of specialized materials and components, highlighting their role in advancing technological infrastructure [5].
Recognizing the importance of sustainable practices, there is a contemporary emphasis on the development of environmentally friendly and waste-free technologies for the production of nitrogen carbonyl compounds [6]. This concerted effort aligns with the global push towards eco-conscious practices, ensuring that the utilization of these compounds aligns with principles of environmental responsibility. As a result, the ongoing research and development in this area hold promise for ushering in a new era of cleaner and more sustainable technologies across diverse sectors of the economy.

2 Materials and methods

The development of ways to synthesize compounds with morpholine fragments and the search for new biologically active substances of this series is an urgent task of modern organic synthesis [7-10].

The significance of morpholine derivatives extends far beyond their basic chemical properties, as they have proven to be integral in various fields such as medicine, pharmaceutics, organic synthesis, and petrochemistry. With a notable presence as tranquillizers, synthetic analgesics, anticonvulsants, and antituberculosis drugs, these derivatives play a crucial role in enhancing therapeutic interventions and pharmaceutical formulations.

In medicine, morpholine derivatives contribute to the development of tranquillizers, providing essential solutions for anxiety and related disorders. Their application as synthetic analgesics underscores their role in pain management, catering to diverse medical needs. Additionally, their presence as anticonvulsants signifies their importance in treating conditions characterized by seizures, offering therapeutic options for neurological disorders.

Pharmaceutics benefits from the versatile nature of morpholine derivatives, where they serve as key components in the synthesis of drugs with diverse pharmacological actions. The continual exploration of new derivatives holds promise for expanding the arsenal of pharmaceutical interventions, addressing a spectrum of health challenges.

Beyond healthcare, these derivatives find application in organic synthesis, contributing to the creation of complex molecules and compounds. In petrochemistry, their utility underscores advancements in refining processes and the synthesis of petrochemical products, showcasing their versatility in the energy sector.

Given the pivotal role of morpholine derivatives across multiple sectors, the ongoing exploration and expansion of their range remain of paramount importance. Both theoretically and practically, the pursuit of new derivatives not only deepens our understanding of molecular interactions but also holds immense potential for unlocking innovative applications in various facets of the national economy.

\[
\begin{align*}
\text{ONH} & + \text{CCH}_2 \text{CCH}_2 \text{Cl} \\
\text{O} & \\
\text{nNOH} & + \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{Cl} \\
\text{O} & \\
\text{Cl}^- & \\
\end{align*}
\]
The study of kinetic regularities of self-polymerization of morpholine with epichlorohydrin was carried out by gravimetric method. To study the influence of the nature of solvents on the polymerization reaction of morpholine with epichlorohydrin, the process was carried out in solvents with different dielectric constant (benzene, acetone, ethanol, dimethylformamide)\[13, 14\].

Based on the results of IR spectral studies and literature data, the structure of the synthesized polymers can be described as follows [4]:

3 Results and discussion

As a result of the studies described above, the technology for obtaining oligomers based on epichlorohydrin and morpholine was proposed. From the technological scheme (Fig. 1) it can be seen that the technology of oligomer production is simplified, the polymerization reaction takes place in the stirred reactor.

Morpholine in ethanol is fed into the upper part of the reactor 1. The reactor 1 is provided with a frame, a stirrer and a jacket for heating or cooling. Epichlorohydrin is then added while stirring.

The loading rates (in mole fractions) of the startup components into reactor 1 are given below:

- Morpholine
- Epichlorohydrin
- Ethanol - 30% vol.

Ethanol is condensed, epichlorohydrin and morpholine go to acceptors 6, 7, 8 respectively. The lower oligomeric layer of the cube is sent for washing. The efficiency of the product is 95-98%.

In ethanol at a molar ratio of 1:1, morpholine and are sent to the top of the reactor where the quaternization and oligomerization reactions take place. The quaternization reaction of morpholine and is carried out under cooling to 0°C; then oligomerization is carried out under gradual heating, temperature first 30°C and then 50°C. The duration of the reaction is 4 hours.

After completion of the reactions, the reaction mixture is directed to the separation column 3 through pump 2. In the column, the easily boiling components, including ethanol and unreacted epichlorohydrin and morpholine, are separated. Ethanol vapor from the top of column 3 enters condenser 4, then condensate receiver 8, and epichlorohydrin and morpholine layers are directed to receivers 7 and 6, respectively.

From the cube of column 3 oligomeric product is obtained, which is sent for purification. The yield of the oligomeric product is 92-95%.

Development of technology for obtaining homopolymers based on \(3\)-chloro-1-morpholizopropylacrylate.

A new technology for the preparation of \(3\)-chloro-1-morpholizopropylacrylate has also been proposed (Fig. 1). Compared to the real thing, it is somewhat simplified, but gives a visualization of the technological process.

\(3\)-Chloro-1-morpholizopropylacrylate readily enters the polymerization reaction in the presence of initiators. Dinitrilazobis-isobutyric acid (DAA) is used as an initiator. Oxygen inhibits the polymerization reaction, so the process is carried out in the presence of nitrogen. Taking into account the experimental results obtained, a schematic diagram of the technological process for the preparation of high-molecular-weight ester based on \(3\)-chloro-1-morpholizopropylacrylate was created.

Synthesis of the polymer product consists of the following steps:

1) preparation and loading of starting reagents (morpholine, EC and water) into reactor 1;
2) synthesis of \(3\)-chloro-1-morpholizopropanol 2;
3) esterification of \(3\)-chloro-1-morpholizopropanol 2 with acrylic acid;
4) rectification of the reaction mass;
5) polymerization reaction of \(3\)-chloro-1-morpholizopropanol 2;
6) purification and drying of the polymer.
1. Basic process flow diagram for obtaining epichlorohydrin oligomer based on morpholine.

2. Recommended loading from MF to sequentially and in the ratio of 1:1 (molar). The synthesis of 3-chloro-1-morpholizopropanol-2 is carried out in a vertical reactor equipped with an anchor stirrer and a heat exchange jacket with brine circulation.

3. The polymerization formulation of 3-chloro-1-morpholizopropylacrylate is shown in Table 1.

4. The technological scheme for the production of poly-3-chloro-1-morpholyl-2-propanol is also proposed (Fig. 2). According to the production technology of the oligomeric product, it consists of the following stages: 1) obtaining 3-chloro-N-morpholyl-2-propanol by chlorohydrogenation reaction; 2) esterification of 3-chloro-N-morpholyl-2-propanol with acrylic acid; 3) separation of the reaction product into fractions by rectification; 4) radical polymerization of 3-chloro-1-morpholizopropylacrylate; 5) purification and drying of the obtained polymer.

5. Reactor 1 is equipped with a stirrer and a cooling jacket. Water, morpholine, epichlorohydrin in the form of a fresh and reversible mixture are fed into the reactor from above (Figure 2).

6. The chlorohydrogenation reaction takes place at -5°C. Duration of the reaction is 10 hours.

7. After completion of the reaction, the obtained product is fed to the rectification column 3 by pump 2 to separate the unreacted part of ECH and MF. The amino alcohol 3-chloro-1-morpholizopropanol-2 from the rectification column together with the inhibitor and acrylic acid goes to the esterifier 8 equipped with a stirrer and a jacket for heating and cooling.

8. Chloro-1-isopropylmorpholyl, having passed through the dosing pump 13 in the esterizer, enters the reactor 14 together with the solvent and initiator. Polymerization Process. The polymerization reactor continues to operate at 60°C after the polymerization process is complete. The polymer product is fed to a washing machine 15 to wash the polymer with ICECAE 2024, 03030 (2024)E3S Web of Conferences https://doi.org/10.1051/e3sconf/202449703030

<table>
<thead>
<tr>
<th>Table 1.</th>
<th>Starting components</th>
<th>Quantity</th>
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<tbody>
<tr>
<td></td>
<td>3-chloro-1-morpholizopropanol-2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Initiator</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Ethanol</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>Acrylic acid</td>
<td>0.5</td>
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9. (#)
fresh acetone. The pressed polymer is dried to a constant weight in a drum dryer. The polymer powder is then fed for stabilization and pelletizing.

Fig. 2.

4 Conclusions

References


