



Polymer communication

Development of ketonic resin by polymerization reaction: A critical review



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ARTICLE INFO

Article history:

Received 4 November 2014

Received in revised form

8 January 2015

Accepted 5 February 2015

Available online 13 February 2015

Keywords:

Ketonic resin

Condensation polymerization

Hydroxyl value

ABSTRACT

Synthetic resins are used for various applications including in paint industry to improve the glossiness, adhesiveness, hardness, and dryness of paints. Resins are essentially polymers, which are built up from simple molecules or monomers and can be prepared mainly by either addition polymerization or condensation polymerization. Ketones and aldehydes can be converted to resinous products by condensation reaction. The desired property of a synthetic resin greatly depends on its method of preparation and its field of application. In this communication, the literature pertaining to the self-condensation of ketones to yield dimer, trimer and tetramer products and also the condensation of various ketone molecules with aldehydes to produce ketone–aldehyde resins are analyzed and a state-of-the-art review is written. The present study provides an overview of: i) effect of various operating parameters like reaction time, temperature, pressure, type of catalyst and its loading on a condensation polymerization reaction; ii) various techniques and ideas to analyze the product properties and to remove the catalyst from the reaction mass; iii) effect of phase transfer catalysts (PTCs) on the resin product properties such as softening temperature, moisture content, Gardner color number etc. In a nutshell, an attempt has been made to get the aforementioned aspects together in a coherent manner so that the information is available at a glance and is expected to be useful to the researchers and for industrial practices.

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1. Introduction

Resin is an organic substance which has wide range of applications including consolidants, adhesives, coatings, casting, molding, and storage materials. Resins play a vital role like excellent chemical resistance, good adhesion properties, heat resistance, oxidative stability, and excellent electrical properties in the field of plastic, textile, electrical and electronics, paper, paint, construction etc. In coating technology, resins are mainly used to provide gloss and elasticity, for suspension of pigments, to provide resistance to water and chemical, besides acting as a dispersant [1].

Broadly, resins are classified as natural resins and synthetic resins based on their occurrence. Natural resins are obtained from trees which exude a viscous liquid when the bark is damaged. Commonly available natural resins are Dammar, Mastic, Rosin, Shellac and Beeswax etc. Natural resins are used for a wide range of

applications like production of perfumes, treatment of bows for instruments such as violins and cellos.

Synthetic resins are essentially polymers, which are built up from simple molecules or monomers. There are two general methods for the production of polymers, namely, addition polymerization and condensation polymerization, and which method to be employed depends on the type of monomer. Common synthetic resins are: alkyd resins, epoxy resins, polyamide resins, polyurethane resins, vinyl resins, polystyrene resins, acrylic resins, phenolic resins, and ketonic resins etc. Most of the natural and synthetic resins are insoluble in water but soluble in organic solvents like propanol, butanol, chloroform, chlorobenzene, cyclohexanone, cyclohexanone, toluene etc. [2].

In this review, we have focused mainly on the polymerization reaction and polymer products from ketones and/or aldehydes to obtain a ketonic resin and its major applications. It is well known that ketones, aldehydes or their mixtures can be converted to resinous products in presence of a base or acid catalyst. Cyclohexanone and formaldehyde react to give hard resins which find use in the coating industry [3].

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Most of the natural resins are quickly affected by caustic potash or caustic soda. Many synthetic resins (e.g. phenol–formaldehyde resin) are also affected by strong alkali. Ketonic resins (obtained from ketone monomer) have the ability to resist caustic alkali and even on boiling the resin with alkali [4]. Ketonic resins can be used in combination with high molecular weight film formers (e.g. cellulose derivatives, chlorinated rubber, vinyl esters, vinyl ethers, vinyl chloride, vinyl aromatics etc.) or chemically drying binders (e.g. alkyd resins) for production of surface coatings and also for making adhesives, printing inks, toner, pigments, varnishes for surface treatment of wood, metal etc. [5,6].

Cyclohexanone ($C_6H_{10}O$) consists of six-carbon cyclic molecule with a ketone functional group. Majority of cyclohexanone is consumed for production of precursors for Nylon–6,6 and Nylon–6 polymer. Cyclohexanone is not carcinogenic in nature but moderately toxic, with a threshold limit value (TLV) of 25 ppm for vapor. Ketonic compound itself offers as an excellent candidate for manufacture of synthetic resin, and has the potential of replacing more hazardous materials like phenolic and aldehyde compounds.

2. Literature review on cyclohexanone polymerization reaction

2.1. Studies on dimer and trimer formation reaction

The most probable dimer products obtained from base catalyzed aldol condensation of cyclohexanone are shown in Fig. 1.

Tsutomu et al. [7] in 1974 studied the self-condensation of cyclohexanone and its methyl substituted derivatives (e.g. 2-methyl cyclohexanone, 2,6-dimethyl cyclohexanone) at a pressure range of 20400–51000 kg/cm²(g) and temperature range of 160–300 °C in the absence of catalyst. Mixtures of dimer, trimer and tetramer products were identified during the course of reaction. IR, NMR and mass spectroscopy instruments were used to identify the products. They identified various products such as 2-(1-cyclohexenyl) cyclohexanone, 2-cyclohexylidene cyclohexanone, 2,6-dicyclohexenyl cyclohexanone, and dodecahydrotriphenylene as a result of self-condensation of cyclohexanone. The reported values of self-condensation of cyclohexanone under various reaction conditions are summarized in Table 1.

The work also reports that the self-condensation of 2-methylcyclohexanone produces around 20 wt.% yield of 2,2-methyl-(2-methylcyclohexenyl) cyclohexanone at 20390 kg/cm² pressure and 200 °C temperature for a reaction time of 1 h. From the results, it can be said that during self-condensation of cyclohexanone under high pressures and temperatures, initially dimer products are formed and then it leads to the formation of trimer, tetramer and polymer products with sufficient reaction time. However, the operations of high pressure process may not be a viable route most of the time and enhanced safety features need to be incorporated in the process.

Joseph et al. [8] in 1976 patented a process for preparation of 2-(1-cyclohexenyl) cyclohexanone by self-condensation of cyclohexanone in presence of Amberlite–200 resin catalyst at a

Table 1
Effect of reaction parameters on self-condensation of cyclohexanone.

Reactant/monomer	Pressure, kg/cm ² (g)	Temp, °C	Time, hr	Yield ^a , wt.%			
				A	B	C	D
Cyclohexanone	20390	200	0.5	5	<1	1	0
Cyclohexanone	20390	250	0.5	1	<1	1	12
Cyclohexanone	35690	200	0.5	7	<1	2	0
Cyclohexanone	35690	250	0.5	1	<1	1	34
Cyclohexanone	45890	200	0.5	1	<1	2	10
Cyclohexanone	45890	250	0.5	1	<1	1	27

^a A = 2-(1-cyclohexenyl) cyclohexanone; B = 2-cyclohexylidene cyclohexanone; C = 2,6-dicyclohexenyl cyclohexanone; D = dodecahydrotriphenylene.

temperature range of 80–110 °C. The reported conversion of cyclohexanone is around 30% with a yield of around 95% of 2-(1-cyclohexenyl) cyclohexanone. However the scope of the process disclosed in the patent is limited to the preparation of dimer products only and is silent about the polymerization products of cyclohexanone.

Muzart [9] in 1982 studied the self-condensation reaction of ketones (cyclopentanone and cyclohexanone) catalyzed by basic aluminium oxide (Al_2O_3) at room temperature. The reaction yielded 2-cyclopentylidene cyclopentanone from cyclopentanone, and cyclohexanone yielded 2-(1-cyclohexenyl)cyclohexanone.

Walter et al. [10] in 1984 disclosed a process on aldol condensation of acetone and other carbonyl-containing compounds using a synthetic clay mineral as catalyst. The general formula of the anionic clay mineral catalyst is: $M_mN_n(OH)_{(2m+2n)} \cdot A_a \cdot bH_2O$, where, 'M' is a divalent metal cation (e.g. Mg^{+2}), 'N' is a trivalent metal cation (e.g. Al^{+3}), 'A' is a mono, di, or trivalent anion (e.g. CO_3^{2-}), 'm' and 'n' are numerical values which vary between 1 and 6, $a = n$, when 'A' is monovalent anion & $a = (1/2)n$, when 'A' is divalent anion, and 'b' is an integer having the values of 1–10. In the work, cyclohexanone was passed through a tubular reactor filled with in-house developed catalyst ($M_6N_2(OH)_{16} \cdot A \cdot 4H_2O$) at a temperature of 300 °C. Gas chromatography technique was used to identify the product compounds. Around 42% conversion of cyclohexanone was identified. The product mixture contained around 13% of 2-(1-cyclohexenyl) cyclohexanone and 24% of 2-cyclohexylidene cyclohexanone.

Jose et al. [11] in 1993 studied kinetics of self-condensation of cyclohexanone in presence of Amberlyst–15 resin catalyst at a temperature range of 70–110 °C. The experiments were conducted in a glass reactor equipped with a mechanical stirrer and reflux condenser with a Dean–Stark apparatus for removal of the condensate water. A mixture of dimer and trimer products such as 2-(1-cyclohexenyl) cyclohexanone, 2-cyclohexylidene cyclohexanone, 2,6-dicyclohexylidene cyclohexanone were obtained during the course of reaction. The concentration of cyclohexanone was measured by gas chromatography (GC) and the moisture content was measured by Karl–Fischer analysis. In the work, the conversion of cyclohexanone was studied at various temperatures and at different catalyst concentrations. The important findings of their study are summarized in Table 2.

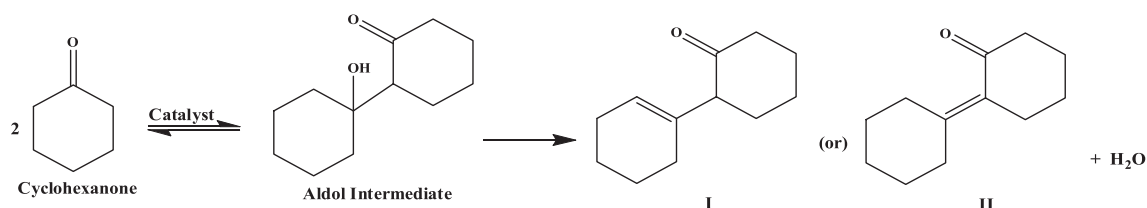


Fig. 1. Reaction scheme of base catalyzed aldol condensation of cyclohexanone. I = 2-(1-cyclohexenyl) cyclohexanone, II = 2-cyclohexylidene cyclohexanone.

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