Liquid Chlorine as Chlorinating Agent for Preparation of Chlorinated Natural and Synthetic Rubbers

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SYNOPSIS

In order to overcome the use of solvents like carbon tetrachloride (during the industrial preparation of chlorinated natural rubber or chlorowaxes) which are suspected of damaging the layer of atmospheric ozone, I proposed the use of liquid Cl_2 as both chlorinating agent and solvent. It is shown that natural rubber or synthetic cis-1,4-polyisoprene can be swelled by liquid chlorine at $-40°C$. By equilibrating to room temperature, the rubber is chlorinated by the expansion of the chlorine trapped in the rubber granules in a process resembling popcorn formation. Chlorine uptake was found to be 56.5% and the chlorinated rubber obtained was studied by FT-IR spectroscopy. Cis-1,4-polybutadiene, when chlorinated with liquid chlorine, gives a hard insoluble product with chlorine content of 36%. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Chlorinated natural rubber is still nowadays an important industrial product since it is commercially available under several trade names like, e.g., Pergut and Alloprene, and it is a thermoplastic powder that is nonflammable and resistant to chemical attack of both acid and basic solutions up to $100°C$.[1] It is used mainly in the formulation of chemical- and heat-resistants paints and coatings by mixing in an opportune solvent at least 10% of chlorinated rubber with plasticizers and pigments.[2,3] Chlorinated rubber is also used in the formulation of adhesives and printing inks.[2,3]

For the industrial preparation of chlorinated natural rubber, batch[4] and continuous processes[5] are now available but in all cases, carbon tetrachloride is used as a solvent for natural rubber to perform the chlorination. In addition, carbon tetrachloride remains as a residue in chlorinated rubber and its removal from the product has been proved to be extremely difficult.[3] Recently, carbon tetrachloride has been banned in all industrial processes in advanced countries since it is suspected (among other things) to damage the the layer of

atmospheric ozone. The easiest approach to replace completely carbon tetrachloride as a solvent in the manufacture of chlorinated rubber (and also in the preparation of other chlorinated products such as chlorinated wax) is to use other chlorinated solvents like, e.g., dichloromethane, chlorobenzene, and o-dichlorobenzene. However, all the above-mentioned solvents have some disadvantages: Dichloromethane can react with chlorine by forming chloroform and carbon tetrachloride and generates hydrochloric acid as a secondary product. Therefore, by recycling dichloromethane after each production cycle, there will be a gradual accumulation of chloroform and carbon tetrachloride in it. On the other hand, monochlorobenzene is flammable, and with o-diclorobenzene, is known to be toxic for the liver and kidneys.[6]

Since we are involved in research in the field of organohalogenated compounds,[7–11] we thought that the radical solution of the problem is to use directly liquid chlorine as a solvent and chlorinating agent in place of all the above-mentioned solvents. This article is an account of our investigation on the subject. The expected advantages are not only the possibility to avoid the use of solvents judged dangerous to humans and to the environment, but also for the absence of solvent residue in the final products.

EXPERIMENTAL

The natural rubber used was SIR-10 purified by dissolving in toluene, filtrating, and precipitating into methanol. Synthetic cis-1,4-polyisoprene was commercially available SKI-3 and prepared over a Ti-based catalyst. High cis-1,4-polybutadiene was obtained from Enichem and was produced over a Nd-based catalyst. The infrared spectra were taken on a Perkin-Elmer FTIR spectrometer 1710 on polymer films cast onto KBr plates from CH_2Cl_2 solutions.

Reaction of Natural Rubber with Liquid Chlorine

Purified natural rubber, 0.20 g, cut into small granules of diameters between 1 and 2 mm were added into a flask containing 3.5 g of liquid chlorine and cooled at $-78°C$ with an external bath of acetone and dry ice. At this temperature, neither dissolution nor reaction between rubber and chlorine was noticed. By increasing the temperature to $-40°C$ (chlorine boils at $-34°C$ at ambient pressure) and maintaining this temperature for 1 h, a certain swelling of the rubber granules was noticed. By leaving the mixture to equilibrate at room temperature, a fast reaction took place with strong swelling of the rubber granules and formation of white vitreous spheres of chlorinated rubber in a process resembling popcorn formation. The yield was 0.46 g, and from this, we can calculate a chlorine content of 56.5%. The chlorinated rubber obtained was completely soluble in dichlorometane, although some gel (no more than 5% by weight) was noticed.

Reaction of Synthetic cis-1,4-Polyisoprene with Liquid Chlorine

Synthetic cis-1,4-polyisoprene, 0.20 g, cut into small granules (1–2 mm diameter), was treated with 3.5 g of liquid chlorine and kept for 1.5 h at $-78°C$. Even at this temperature, a certain swelling of the rubber granules was noticed. After another hour at about $-40°C$, the reaction mixture was allowed to equilibrate at room temperature. A very strong swelling with formation of vitreous spheres of chlorinated rubber was recorded. The yield was 0.45 g and, hence, chlorine uptake was 55.5%. Also, here the product was completely soluble in dichloromethane with a gel content of about 5% by weight.

Reaction of cis-1,4-Polybutadiene with Liquid Chlorine

Cis-1,4-polybutadiene, 0.48 g (cut into granules as above), was treated with 4.0 g of liquid chlorine as described above. Very low swelling was noticed at low temperature, and after equilibrating at room temperature, hard whitish granules were recovered with a very low degree of swelling. The yield was of 0.75 g, so that the chlorine content was about 36%. This product was completely insoluble in dichloromethane.

RESULTS AND DISCUSSION

The idea to use liquid chlorine as a solvent and chlorinating agent is not new, since we were able to find old patents on the subject dating back 1937.[12,13] But at that time when these patents were filed there were easier and more economical processes available and, in addition, the sensitivity toward environmental problems was not at today's levels; therefore, these patents probably have never been carried out.

Our experimental data show that preparation of chlorinated rubber from natural and synthetic cis-1,4-polyisoprene with liquid chlorine is a feasible process which is governed essentially by the diffusion of chlorine inside the solid rubber granule. By working at $-78°C$, i.e., below the glass transition temperature of cis-1,4-polyisoprene which lies at about $-65°C$, the diffusion process of chlorine into the solid rubber granule is very low because the rubber is in a glassy state. By approaching a temperature of $-40°C$, near the boiling point of liquid chlorine at ambient pressure ($-34°C$), the diffusion process becomes appreciable (also because now we are above the glass transition temperature of the rubber, and, hence, the rubber is in a rubbery state); consequently, a neat swelling of the rubber granules can be noticed. By heating the swelled rubber to room temperature, the chlorine trapped inside it becomes gaseous and, under pressure, chlorinates the rubber granule with the formation of glassy spheroidal granules in a process resembling that of popcorn formation.

Industrially, the chlorination of natural or synthetic cis-1,4-polyisoprene could be conducted as described by using low temperatures and then by reequilibrating at room temperature and recycling the unreacted chlorine. However, a more attractive alternative could be to use liquid chlorine under a pressure of only 6.6 atm at 20°C. In this manner, chlorination should be very fast and effective, the diffusion of chlorine into the solid rubber granules (or the milled thin sheets) being governed by the overpressure applied to maintain chlorine in the liquid state, while the chlorination should take place easily, as is well known, at room temperature.
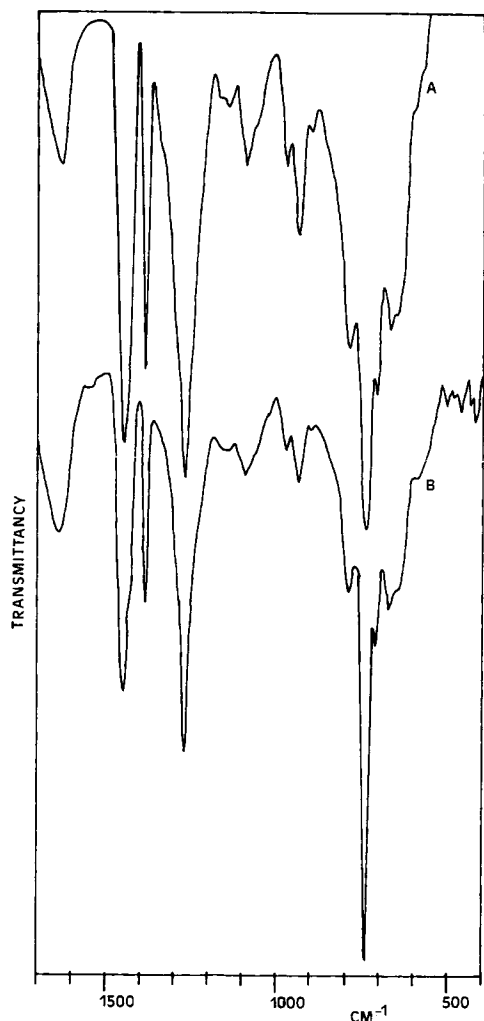
Figure 1 (A) FTIR spectrum of chlorinated synthetic cis-1,4-polyisoprene. (B) FTIR spectrum of chlorinated natural rubber.

In Figure 1, we report the FTIR spectra of the chlorinated rubber prepared from natural and synthetic cis-1,4-polyisoprene using liquid chlorine. The extensive and almost complete chlorination is indicated by the bands at 788, 706, 738, 668, and 640 cm^{-1}, all due to C—Cl stretching. Moreover, the strong band at 830 cm^{-1} present in the starting polymer and due to cis ==C—H bending has completely disappeared in the spectrum of the chlorinated product obtained. If we compare the infrared spectra of chlorinated rubber obtained in the present work with liquid chlorine with that of the same product obtained according to the classical route in

carbon tetrachloride,[7] we may notice that they are comparable. Consequently, the structure of the products obtained through different methods of preparation are almost comparable. Elsewhere, other scientists have discussed the structure of chlorinated cis-1,4-polyisoprene.[14-17]

A separate discussion is needed for the chlorination of cis-1,4-polybutadiene. Despite the chlorination with liquid chlorine being conducted at temperatures well above the glass transition temperature of this polymer (which lies at −103°C), the diffusion of chlorine into its granules remains always very low and extensive crosslinking and cyclicization takes place by heating up to room temperature so that the product obtained is even insoluble in dichloromethane. We may note that chlorinated polybutadiene preparable with conventional methods has never been commercialized.

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