

# Synthesis of a novel polymer via the coupling reaction of cyanuric chloride and a di-amine

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## ***Abstract:***

Polymers containing hydrogen bonds are of great significance as they have the potential to strengthen the mechanical properties of a material through non-covalent crosslinking, which is the basis for paint and self-healing materials. In this work we describe a method to obtain a novel polymer via the coupling reaction of cyanuric chloride and a di-amine. We investigate the reaction conditions to optimise the polymerization yield and molecular weight polydispersity. The polymerization process was characterised by gel permeation chromatography (GPC), nuclear magnetic resonance spectroscopy (NMR), and attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectrometry.

***Keywords:*** cyanuric chloride, di-amine, hydrogen bond, triazine.

***Classification number:*** 2.2

## **Introduction**

There is a growing interest in synthetic polymers with strong non-covalent crosslinking that induces ionic,  $\pi$ - $\pi$  stacking, and hydrogen bonding. This type of polymer is applied across many fields from paint to recycled and self-healing materials. In this article, we synthesised a polymer with hydrogen interaction by cyanuric chloride and amine. The attractive interaction between a high-electron-density atom and an electron-deficient hydrogen gives rise to hydrogen bonding [1, 2]. A hydrogen bond forms when an electron is moved from a proton acceptor (such as N, F, O atoms) to a proton donor molecule (i.e. electron-deficient hydrogen). Although hydrogen bonds are weaker than polar and covalent bonds, they are stronger than the van der Waals forces [3]. Thus, one can use hydrogen bonding to effectively enhance the mechanical properties of a material.

Polymerization of cyanuric chloride with a di-amine is used to introduce a triazine ring and NH group to the polymer backbone. Hydrogen interactions can form between the proton-acceptor of the triazine ring and the proton-donor of the NH group. This hydrogen bond in the triazine ring is popularly used. When the coupling reaction of cyanuric chloride with the di-amine occurs, the obtained polymer backbone has one nitrogen atom acceptor and two amino hydrogen donors next to each other. This structure can form a stronger hydrogen bond [4]. Therefore, the triazine ring is

introduced into the polymer chain using a coupling reaction to cyanuric chloride.

Cyanuric chloride is known as a multifunctional reactive dye and can be completely controlled by temperature. The chlorine atoms of cyanuric chloride are easily replaced by other nucleophilic agents in the presence of a hydrochloride electron acceptor. The chlorine substitution is temperature controlled step by step, has been observed to follow an empirical rule: mono chlorine replacement occurs at a temperature of 0°C or lower, di-chlorine at room temperature, and tri-chlorine at temperatures above 60°C [5].

This synthetic process is an easy polymerization technique to create triazine-based polymers with hydrogen bonding interactions. Moreover, the reaction of cyanuric chloride with a di-amine is efficient and gives a high yield.

## **Materials and methods**

### ***Materials***

The polypropylene oxide di-amine (PPO di-amine) was purchased from Sigma Aldrich with molecular weight of 2000 g/mol, cyanuric chloride (99%) and N,N-Diisopropylethylamine (DIPEA, 99%) were bought from Sigma Aldrich and the solvents were received from Fisher Chemicals.

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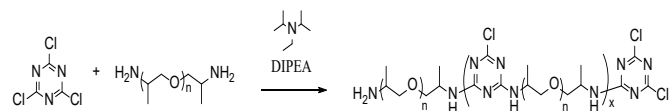
### Characterisation

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were measured at 300 MHz using a Bruker Avance 300 with deuterated acetone ( $\text{C}_3\text{D}_6\text{O}$ ) and tetramethylsilane internal reference. Attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectra of the polymers were measured at  $4\text{ cm}^{-1}$  resolution using an FT-IR Tensor 27 spectrometer with a diamond/ZnSe element combined with a Pike MIRacle ATR accessory. Gel permeation chromatography was recorded on a Polymer PL-GPC 50 gel permeation chromatograph system with a refractive index (RI) detector. Chloroform was used as the eluent and the flow rate was 1.0 ml/min. Polystyrene standards were used for the calculation of the molecular weight and molecular weight distribution.

### Synthesis of polymer triazine

Cyanuric chloride 1.0 g (5.42 mmol) was added to 27.1 ml of the tetrahydrofuran solvent in a two-neck flask. Polypropylene oxide di-amines 2.3 g (5.42 mmol) and *N,N*-diisopropylethylamine 2.1 ml (1.5 g, 11.93 mmol) was then added to the flask. The reaction was kept under constant stirring for 24 h at room temperature. Then, the solid was removed by filtration and the polymer, in liquid form, was collected.

### Results and discussion



Scheme 1. Synthesis of polymer triazine.

The polymerization process described in Scheme 1 is the reaction of the primary amine with cyanuric chloride. At room temperature, the first and second reactive positions on cyanuric chloride react, while a temperature of  $60^\circ\text{C}$  or higher is needed to activate the third reactive site [6]. The above polymerization process was maintained at room temperature so that the polymer backbone was extended instead of forming a network. The molecular weight of the polymer was observed by the GPC curve in Fig. 1, where the number averaged molecular weight ( $M_n$ ) is approximated at

11090, the molecular weight ( $M_w$ ) is approximated at 15160, and the high PDI ( $M_w/M_n=1.36$ ) is likely due to the coupling reaction, since the number of repetitions of the unit in the polymer cannot be controlled.

The polymer triazine was synthesised with the catalyst DIPEA as shown in Scheme 1, so that the peak at 1.4 ppm for the  $\text{CH}_3$  group in DIPEA appeared in the  $^1\text{H}$  NMR spectrum of the polymer, as seen in Fig. 2. The disappearance of the  $\text{NH}_2$  group in the  $^1\text{H}$  NMR spectrum of polypropylene oxide di-amines (2.6-3 ppm, Fig. 3) can be observed, which indicates that all  $\text{NH}_2$  groups reacted with the cyanuric chloride. The appearance of peak d (6.3-6.7 ppm, Fig. 2) corresponding to the NH groups were created.

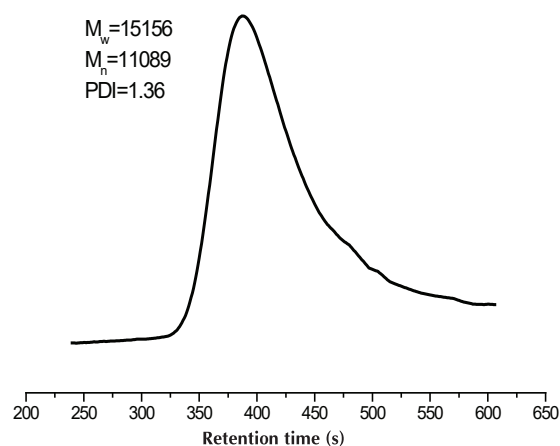


Fig. 1. GPC of polymer triazine.

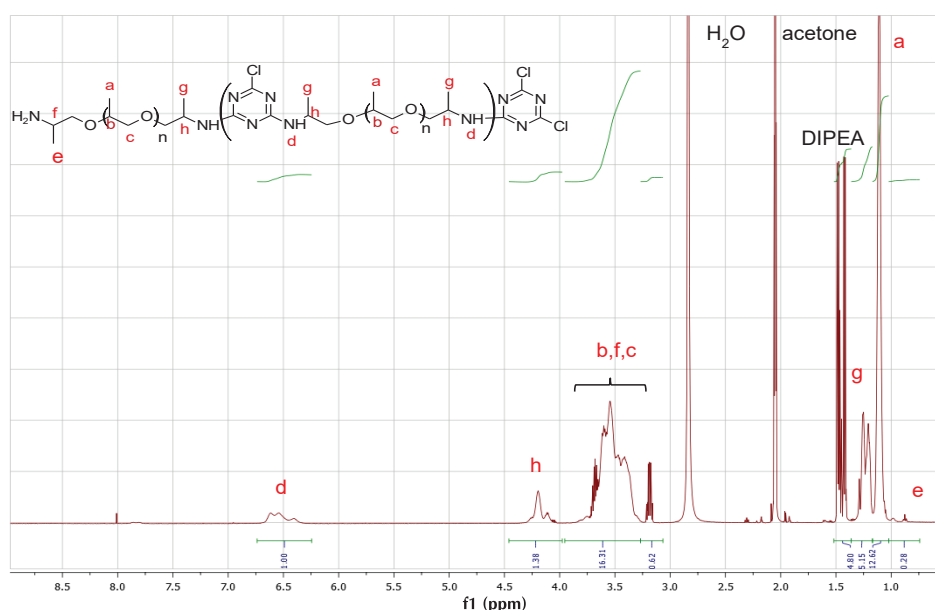


Fig. 2.  $^1\text{H}$  NMR spectrum of polymer triazine in acetone.

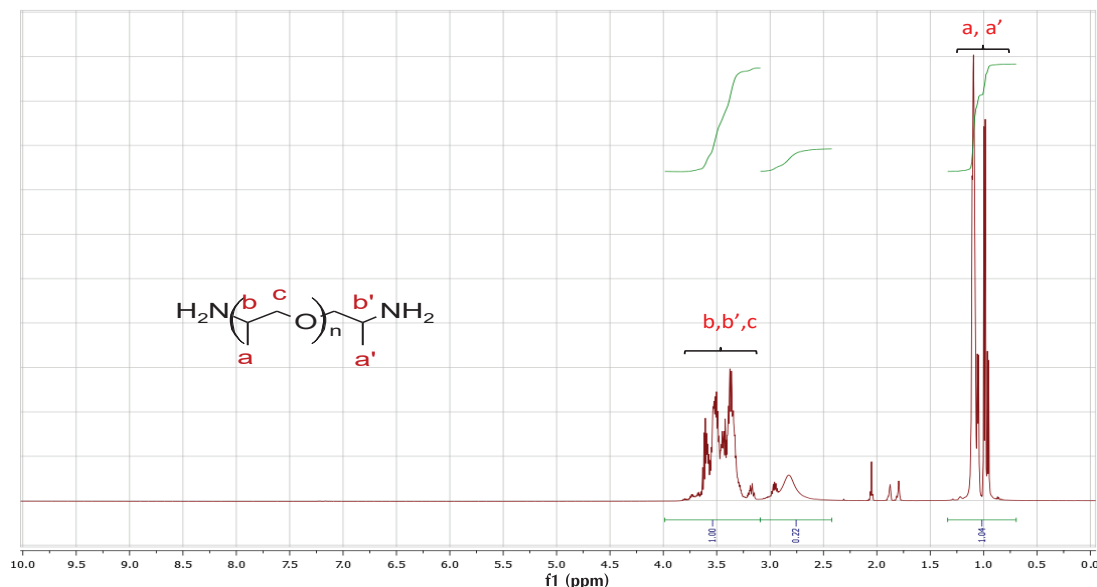


Fig. 3.  $^1\text{H}$  NMR spectrum of polypropylene oxide di-amines in  $\text{CDCl}_3$ .

From the FT-IR spectra of cyanuric chloride, polypropylene oxide di-amines, and the polymer in Fig. 4, the characteristic absorption bands of cyanuric chloride at  $1171$  and  $1265\text{ cm}^{-1}$  assigned to the triazine stretch [7] and the bands at  $844\text{ cm}^{-1}$  corresponds the C-Cl stretch vibrational absorption [8] can be observed. After the coupling reaction, the band for the C-Cl stretch at  $844\text{ cm}^{-1}$  in FT-IR spectrum of polymer disappeared. The appearance of the peak at  $1571\text{ cm}^{-1}$  was due to N-H secondary amine in reaction.

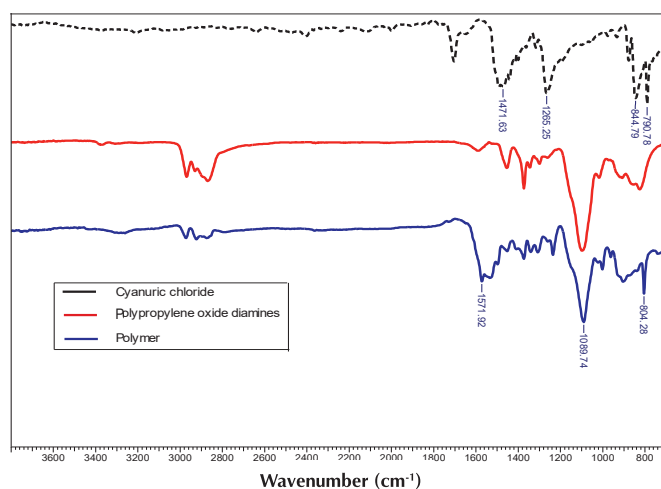


Fig. 4. ATR FT-IR spectra of cyanuric chloride, polypropylene oxide di-amines and polymer triazine after synthesis.

## Conclusions

In conclusion, the triazine-based polymer capable of hydrogen interaction was successfully synthesised by the coupling reaction of cyanuric chloride with a di-amine. The structure of the polymer and the appearance of hydrogen bonding were clarified by ATR FT-IR and  $^1\text{H}$  NMR. Moreover, the modification processes to attach more proton donors and acceptors are currently under further study.

## ACKNOWLEDGEMENTS

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The authors declare that there is no conflict of interest regarding the publication of this article.

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