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## Synthesis and Characterization of Trichlorophenol-blocked Polyaryl Polyisocyanate

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### ABSTRACT

Typical blocked isocyanate systems are used to obtain the performance of two-component polyurethane system in a one-component mixture. In this study a blocked adduct was synthesized by 2,4,6-trichlorophenol (TCP) as blocking agent for polyaryl polyisocyanate (PAPI). This blocking reaction was in the presence or absence of the catalyst (dibutyltin dilaurate, DBTDL). Elimination of the isocyanate groups and the formation of urethane bonds were studied by FTIR spectroscopy and titration methods. FTIR Spectrum indicates that the NCO groups of the isocyanate molecule are blocked with TCP and the added catalyst should make the reaction faster than that of un-added catalyst. The blocked adduct was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, DSC and TG/DTA. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of blocked adduct demonstrated that the structure of the carbamate was observed. Thermal dissociation of blocked diisocyanates was analyzed by DSC and TG/DTA techniques. Deblocking temperature obtained by DSC and TG/DTA techniques was compared. Based on DSC data, it was found that deblocking of blocked PAPI started at 75°C. In general, TG/DTA results showed the same trend as DSC. Deblocking temperature value obtained by TG/DTA technique was lower than DSC value. Differential thermal analysis showed the blocked PAPI began to deblock at 70°C.

### Key Words:

blocked isocyanate;  
trichlorophenol;  
polyaryl polyisocyanate;  
deblocking temperature;  
polyurethane.

### INTRODUCTION

Polyurethanes are versatile polymers that contain the carbamate structure (-NH-CO-O-). Polyurethane chemistry as well as the chemistry of related intermediates has been utilized enormously to develop many products in the form of fibres, soft and hard elastomers, foams, skins, adhesives, binders, coating for many purposes and highly cross-linked plastics [1]. A rapid reaction between a multifunctional isocyanate and a hydroxyl or amine terminated

oligomer leads to formation of urethane bond. The high reactivity and toxicity of isocyanates do not allow their storage and use in one-component systems, and their reactions are rarely devoid of undesirable side reactions. For this reason, protecting the isocyanate against moisture and self-addition reaction is difficult. Such problems associated with isocyanates have been satisfactorily overcome by blocking them with a compound containing an active hydrogen atom,

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blocking agent, through the formation of carbamate having a labile bond which can dissociate at a higher temperature to regenerate isocyanate and blocking agent functionality [1-4]. The reaction can be seen as:



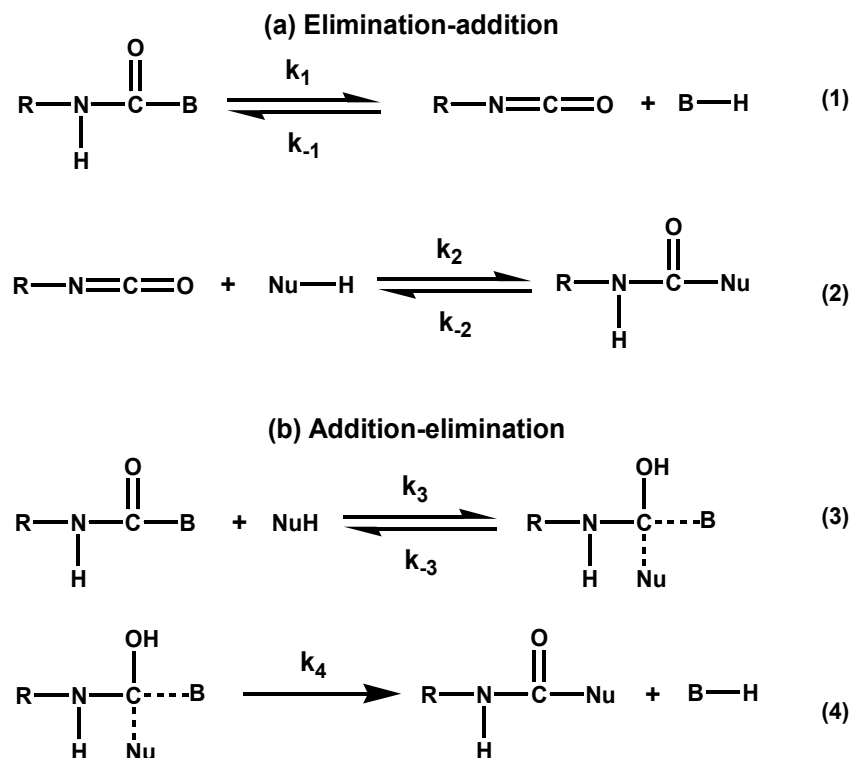
where B-H is the blocking agent.

It is well known that there are two urethane forming reaction mechanisms by which a blocked isocyanate can react with a nucleophile (NuH). In the elimination-addition reaction (Scheme Ia), the blocked isocyanate decomposes to the free isocyanate and the blocking group (BH). The isocyanate then reacts with a nucleophile to form a final product. In addition-elimination reaction (Scheme Ib), the nucleophile reacts directly with the blocked isocyanate to yield a tetrahedral intermediate followed by elimination of the blocking agent [5-7].

The most widely used commercial blocking agents are phenols, pyridinols, thiophenols and mercaptopyridines; alcohols, other hydroxy-functional

agents, and mercaptans; oximes; amides, cyclic amides, and imides; imidazoles, amidines, and related compounds; pyrazoles and 1,2,4-triazoles; amines; active methylene compounds and other blocking agents [8-18]. The high deblocking temperature can be advantageous in some applications. For example, pyrrolidone-blocked TMI is desirable as a monomer in making blocked isocyanate-functional synthetic rubber since it does not deblock at temperatures below about 160°C. Thus, the rubber is less likely to scorch during processing before vulcanization due to cross-linking [19-21]. Furthermore, there are certain application areas for which it is necessary to use a blocking agent that should be cleaved off at temperatures less than 100°C (e.g., solid rocket propellant, which contains explosive material [1]; wood processing, etc.). At present, the blocked isocyanate of lower deblocking temperature is the oxime blocked monomer. But its deblocking temperature is 100°C or so [2,5].

Due to the high deblocking temperature, general blocked-isocyanates are unsuitable for some important applications such as one-component aqueous polymer isocyanate adhesives. Recently, our



Scheme I. Mechanism of blocked isocyanate.

group has studied a low temperature deblockable blocked-isocyanate and found that the deblocking temperature of TCP as blocking agent for PAPI is markedly lower than that of phenol as blocking agent. The reason is that deblocking temperature of the blocked isocyanates depends on the structures of the blocking agents and structures of the isocyanates. Substituents present in the phenolic aromatic ring with electron-withdrawing tendency decrease the deblocking temperature while electron releasing groups increase the deblocking temperature [1]. In this study, the blocking agent (TCP) has three strong electron-withdrawing groups, chlorine atom, in the *ortho*- and *para*- to the phenolic hydroxyl, which make it more activated. Further, no detailed literature report is available. In this paper, it is reported that the blocked adduct was synthesized by using TCP as a blocking agent for PAPI and characterized by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DSC and TG/DTA.

## EXPERIMENTAL

### Materials

The raw materials used in this study are listed in Table 1. All these materials are laboratory grade chemicals and solvents are purified according to standard procedures.

### Preparation of Blocked Polyaryl Polyisocyanate

A 250-mL three-necked flask equipped nitrogen inlet, condenser was charged with TCP, DMF and PAPI. An appropriate amount according to the desired  $[\text{NCO}]/[\text{OH}]$  ratio was taken in the reaction kettle. The reactants were heated to  $80^\circ\text{C}$  in a constant temperature bath. The change in NCO content during reaction was determined using a standard dibutylamine back titration method [22]. The reaction time was 3 h, and the blocking agent was added either in one-time fashion or dropwise, whether the addition of catalyst, dibutyltin dilaurate (DBTDL), depends on the situation.

### Measurements

Quantitative analysis of NCO mass fraction: using a standard di-n-butylamine method.

Qualitative analysis of NCO mass fraction: 1-2

drop blocked isocyanate was charged into a beaker and dispersed uniformly with solvent. Then, several drops of aniline were added and shaken up. Finally, by observing for any deposition the mixture remained quietly for 15 min. There would be deposition unless the blocking reaction was uncompleted [22].

Fourier transform infrared spectroscopy: Fourier transform infrared (FTIR) spectrometer (Spectrum One, PE Corporation, USA) was used to examine chemical structure of blocked isocyanate. The FTIR spectra were recorded with a spectral range of  $4000$  to  $400\text{ cm}^{-1}$ .

Differential scanning calorimetry (DSC) measurement: DSC was used to examine the thermal behaviour of blocking isocyanate, differential scanning calorimetry (DSC 204F1, Netzsch, Germany). DSC measurement was scanned at a heating rate of  $10^\circ\text{C}/\text{min}$ , with a temperature range of  $20$  to  $300^\circ\text{C}$ .

Differential thermal analyses (DTA): differential thermal analyses were carried out with Damiand TG/DTA analyzer (PE Corporation, USA). The sample weight was 8-10 mg. The work was performed from  $20$  to  $410^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

Nuclear magnetic resonance (NMR):  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in DMSO on a Bruker AV400 spectrometer, working at  $400.13\text{ MHz}$  and  $100.61\text{ MHz}$ , respectively.

## RESULTS AND DISCUSSION

One drawback of isocyanates is the excessive moisture sensitivity of the NCO group, which could lose its functionality upon storage. A possible solution is to mask this functional group with a blocking agent which can be thermally removed before use. In a preceding work of ours it was demonstrated that TCP-blocked PAPI can be deblocked at lower temperature.

### FTIR Analysis

PAPI was blocked with stoichiometric equivalent of the blocking agent, TCP, to get blocked adduct. The NCO group has characteristic absorption peak at around  $2250$ - $2270\text{ cm}^{-1}$  which is due to the antisymmetric stretching. FTIR Spectra of PAPI and TCP-blocked PAPI adduct are depicted in Figure 1.

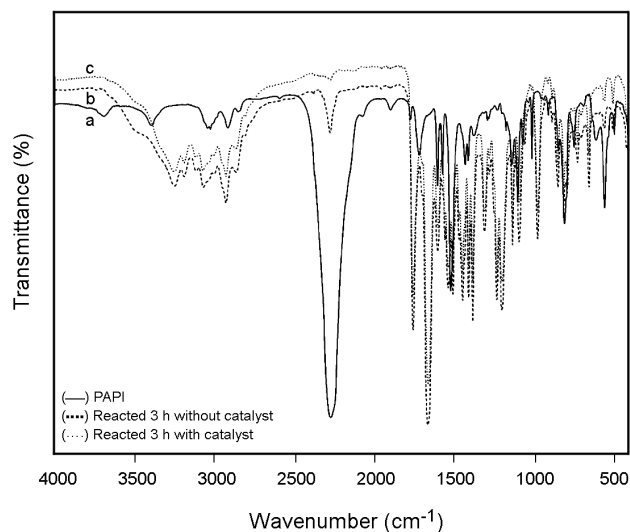
**Table 1.** Raw materials used.

Designation	Chemical structure	Chemical description	Suppliers
PAPI	<p style="text-align: center;"><math>n=0,1,2,3</math></p>	Polyaryl polyisocyanate	ICI Company (Britain)
TCP		2,4,6-Trichlorophenol	Alfa Aesar (China)
DMF		<i>N,N</i> -Dimethylformamide	Tianjin Kermel Chemical Reagent Co., Ltd. (China)
MB		Toluene	Changchun Chemical Reagent Plant (China)
MEK		Butanone	Tianjin Kermel Chemical Reagent Co., Ltd. (China)
Ethanol		Ethanol	Tianjin Kaitong Chemical Reagent Co., Ltd. (China)
di- <i>n</i> -Butylamine		di- <i>n</i> -Butylamine	Tianjin Kaitong Chemical Reagent Co., Ltd. (China) SCRC (China)
Aniline		Aniline	Tianjin Bodi Chemical Co., Ltd. (China)
<i>o</i> -Toluidine		<i>o</i> -Toluidine	Shanghai Tingxing Chemical Reagent (China)
DBTDL		Dibutyltin dilaurate	Tianjin Kermel Chemical Reagent Co., Ltd. (China)

The NCO absorption peak at  $2270\text{ cm}^{-1}$  was seen to diminish sharply when the reaction was carried out for 3 h, while it was nearly disappeared with catalyst at the same time. This indicates that the NCO groups of the isocyanate molecule are blocked with TCP and the catalyst should have accelerated the reaction. As indicated earlier, there are many reactions taking place and the catalyst can be involved in one or some

of them [5]: (i) the deblocking reaction, or, (ii) the reaction of the free isocyanate with the other nucleophile, or, (iii) an addition-elimination reaction, and/or, (iv) side reactions.

At present, it is well accepted that the catalyst can be involved in an addition-elimination reaction. The most commonly used tin-based catalyst is dibutyltin dilaurate, being a typical catalyst for the reaction of



**Figure 1.** FTIR Spectra of: (a) polyaryl polyisocyanate; (b) TCP-blocked polyaryl polyisocyanate without and (c) with catalyst.

free isocyanates with amino- and hydroxyl-nucleophiles. DBTDL leads to strongly enhanced reaction rates, but the deblocking temperatures decrease not as strong in comparison to many metal dionates or metal oxides [23]. Firstly, DBTDL forms a complex with isocyanate and makes it polarize, where C atom of NCO group shows positive charge; further,  $C^+$  combines easily with the phenolic

hydroxyl group of 2,4,6-TCP to obtain an extraordinarily unstable complex and finally, carbamate would be produced via resetting this unstable complex [24]. The catalysis reaction is presented in Scheme II.

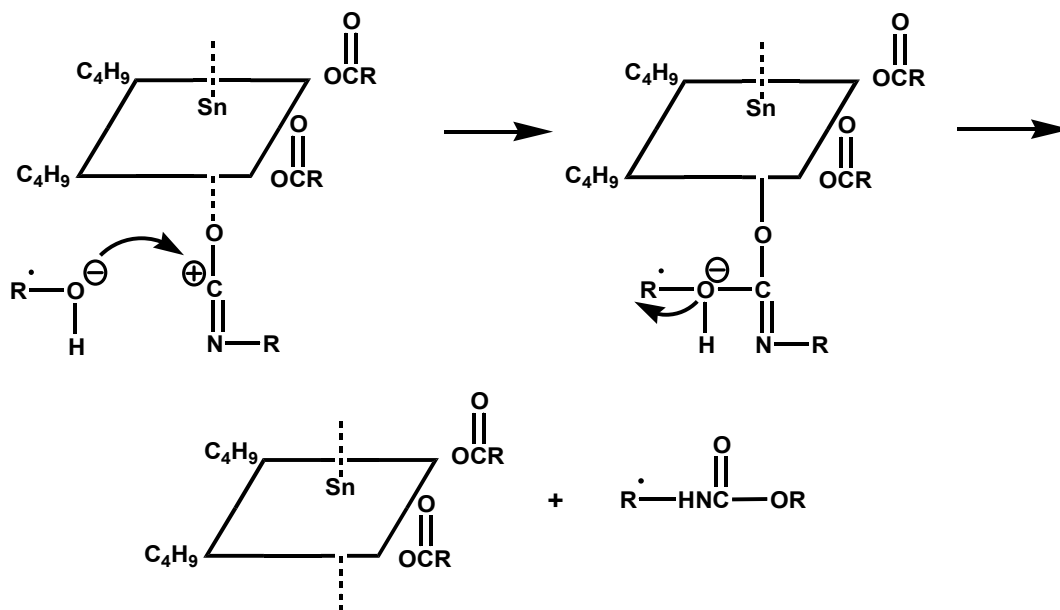
In Figure 1, strong absorptions at  $1700\text{ cm}^{-1}$  (C=O stretching),  $3250\text{--}3300\text{ cm}^{-1}$  (N-H stretching),  $1530\text{--}1560\text{ cm}^{-1}$  (N-H bending) and  $1210\text{--}1240\text{ cm}^{-1}$  (the stretching vibration of the C=O group of urea combined with the N-H group) [8] confirm the formation of blocked polyisocyanate adducts.

### NMR Analysis

Typical  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of blocked polyisocyanate are given in Figures 2 and 3, respectively.

Figure 2 shows the  $^1\text{H}$  NMR spectrum of the TCP-blocked PAPI. Therefore, the blocked adduct was dissolved in hot  $\text{DMSO-d}_6$  ( $\sim 2\text{ mg}\cdot\text{mL}^{-1}$ ). The urethane signal is found at 7.86 ppm. The signals of the methylene protons adjacent to the phenyl group are found at 3.86 and 2.06 ppm. Because of the uncompleted blocking reaction, a phenolic hydroxyl group is observed at 8.32 ppm. All other phenyl protons are found at high field between 7.1 and 7.5 ppm.

The  $^{13}\text{C}$  NMR spectrum of TCP-blocked PAPI along with the assignments is shown in Figure 3. The appearance of a strong peak at 40 ppm belongs to



**Scheme II.** Catalysis of dibutyltin dilaurate.

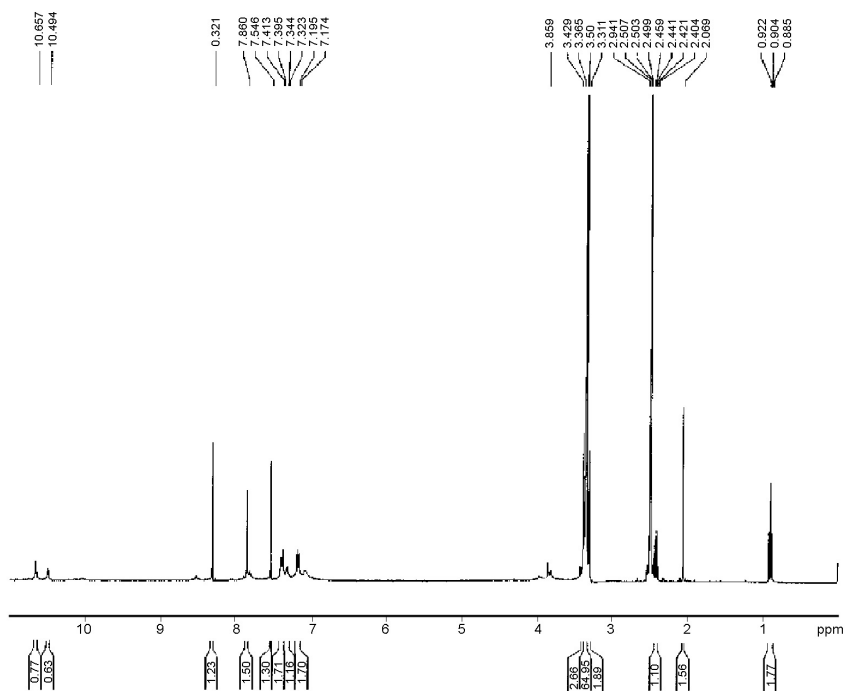


Figure 2. <sup>1</sup>H NMR Spectrum of TCP-blocked polyaryl polyisocyanate.

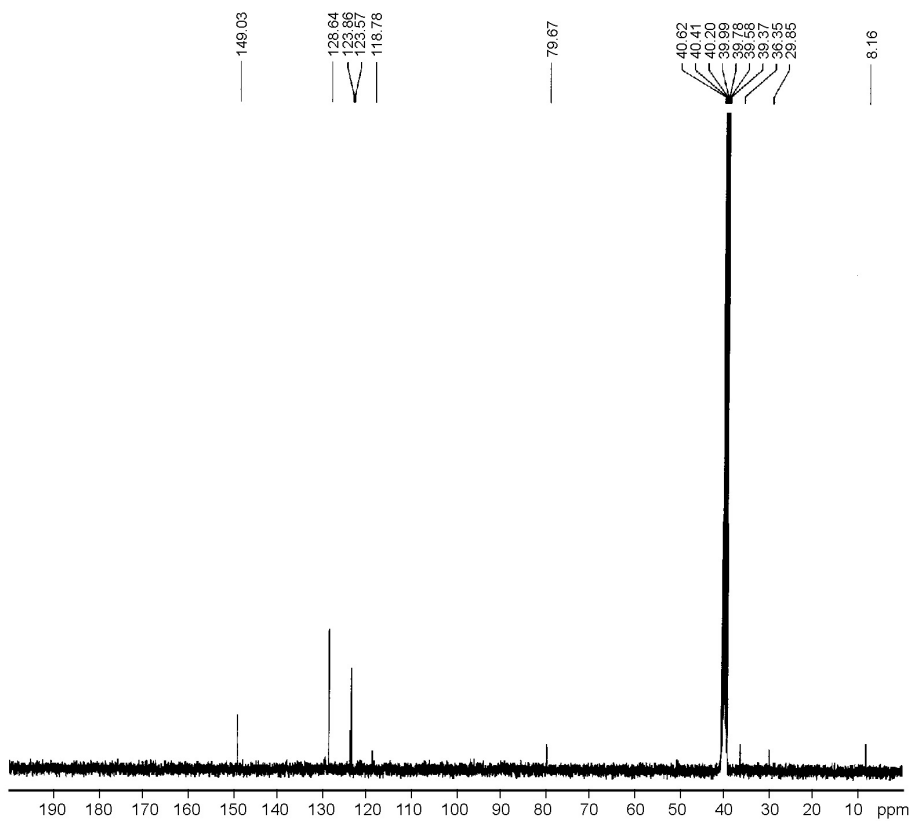


Figure 3. <sup>13</sup>C NMR Spectrum of TCP-blocked polyaryl polyisocyanate.

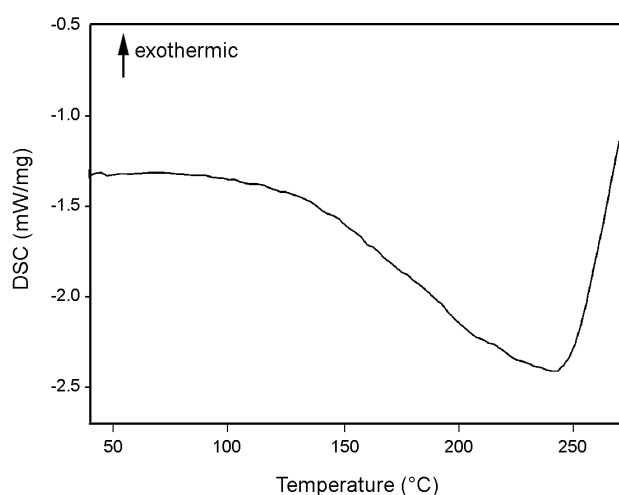
solvent. The chemical shift assignments of various carbon atoms are based on the additivity constants for substituted benzene. The peak due to carbonyl carbon of the carbamate is observed at 149 ppm. This confirms the formation of TCP-blocked isocyanates and their structures. The methylene carbon has peak at 36 ppm. The other peaks are due to the aromatic ring carbons of this adduct.

### Thermal Properties

#### DSC Analysis

The DSC curve is shown in Figure 4. The dissociation of the blocked isocyanate seems due to the fracture of -NH-CO- chemical bond. When endothermic fracture of chemical bond happens, the temperature can be represented as the initial dissociation temperature [4]. DSC Curve of TCP-blocked PAPI demonstrated broad endotherm, which is due to the deblocking of blocking agent. The broad deblocking temperature range may be due to slow and controlled release of blocking agent [8]. TCP-blocked PAPI adduct deblocks at about 75°C, which is lower than those of other blocking agents of blocked PAPI that was reported in the literature [25]: MEKO-blocked PAPI adduct > 140°C; phenol-blocked PAPI adduct > 120°C.

In Figure 4, there is one endothermic peak, that is TCP-blocked PAPI possessing one functional group on its molecule, a blocked isocyanate group, which may regenerate isocyanate group at an elevated



**Figure 4.** DSC Curve of TCP-blocked polyaryl polyisocyanate.

temperature. The minimum dissociation temperature of the blocked adduct is about 75°C.

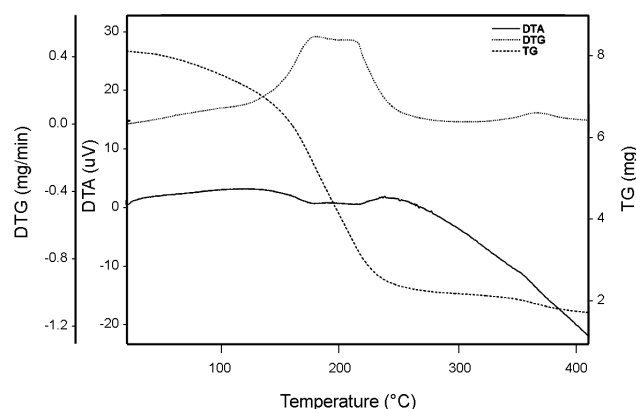
#### TG/DTA Analysis

The thermal stability of the polymer is investigated by TG/DTA. The thermograms of TCP-blocked PAPI are depicted in Figure 5. TG/DTA measures the changes in sample weight over a specified temperature range. Thus, TG/DTA is unsuitable for compounds that do not exhibit volatility over the unblocking temperature range. In order to obtain the pure deblocking temperature of TCP-blocked PAPI, no catalyst was being used for the reaction. The TG/DTA thermograms of TCP-blocked PAPI adduct show that the blocked adduct dissociates at 70°C, which is more or less in agreement with the result of DSC analysis. From Figure 6, half of the blocked adduct has been deblocked around 170°C. In general, the deblocking temperature would be dropped when the blocked adduct is in polar solvents [26].

It is reported that the deblocking temperatures of commercial blocked-isocyanates are as follows [2,5]:

- (i) MEKO-blocked TDI adduct > 108°C, (ii) caprolactam-blocked TDI adduct > 130°C, (iii) MEKO-blocked MDI adduct > 120°C, (iv) caprolactam-blocked MDI adduct > 158°C, (v) DMP (3,5-dimethylpyrazole)-blocked TDI adduct > 75°C, and (vi) DMP-blocked MDI adduct > 105°C.

Differential thermal analysis shows the same trend as DSC. Deblocking temperature value obtained by TG/DTA technique is lower than DSC value. TG/DTA analysis shows that TCP-blocked PAPI



**Figure 5.** TG/DTA Thermograms of TCP-blocked polyaryl polyisocyanate.



adduct begins to deblock at 70°C, which is lower than that of commercial blocked-isocyanates reported earlier. The conformable temperature of wood processing is controlled about 100°C so that TCP-blocked PAPI adduct should be of commercial importance.

## CONCLUSION

Under mild reaction conditions, a novel blocked isocyanate adduct was synthesized from 2,4,6-trichlorophenol with polymethylene polyphenyl isocyanate. FTIR Spectrum indicates that the NCO groups of the isocyanate molecule are blocked with TCP and the DBTDL should have speeded the reaction markedly.

The advantage of this approach is the low deblocking temperature of blocked-PAPI. Based on DSC data, it was found that deblocking of blocked PAPI started at 75°C. In general, TG/DTA results showed the same trend as DSC. Deblocking temperature value obtained by TG/DTA technique was lower than DSC value. Differential thermal analysis showed that the blocked adduct began to deblock at 70°C. These two deblocking temperatures were both lower than those of reported commercial blocked-isocyanates.

## ACKNOWLEDGEMENT

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## SYMBOLS AND ABBREVIATIONS

TCP : 2,4,6-Trichlorophenol  
 PAPI : Polyaryl polyisocyanate  
 NuH : Nucleophile  
 TMI : 1-(1-Isocyanato-1-methylethyl)-3-(1-methylethenyl)-benzene  
 DMF : Dimethyl formamide  
 DBTDL: Dibutyltin dilaurate

FTIR : Fourier transform infrared  
 DSC : Differential scanning calorimetry  
 DTA : Differential thermal analysis  
 NMR : Nuclear magnetic resonance  
 DMSO : Dimethyl sulphoxide  
 MEKO : Methyl ethyl ketoxime  
 TDI : Toluene diisocyanate  
 MDI : Methylene di(phenylene isocyanate)  
 DMP : 3,5-Dimethylpyrazole  
 Me : Methyl  
 Bu : Butyl

## REFERENCES

1. Sankar G, Nasar AS, Effect of isocyanate structure on deblocking and cure reaction of *N*-methyl-aniline-blocked diisocyanates and polyisocyanates, *Eur Polym J*, **45**, 911-922, 2009.
2. Subramani S, Park YJ, Lee YS, Kim JH, New development of polyurethane dispersion derived from blocked aromatic diisocyanate, *Prog Org Coat*, **48**, 71-79, 2003.
3. Gnanarajan TP, Iyer NP, Nasar AS, Radhakrishnan G, Preparation and properties of poly(urethane-imide)s derived from amine-blocked-polyurethane prepolymer and pyromellitic dianhydride, *Eur Polym J*, **38**, 487-495, 2002.
4. Yin LG, Liu YL, Ke Z, Yin JH, Preparation of a blocked isocyanate compound and its grafting onto styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene triblock copolymer, *Eur Polym J*, **45**, 191-198, 2009.
5. Wicks DA, Wicks Jr. ZW, Blocked isocyanates III: Part A. Mechanisms and chemistry, *Prog Org Coat*, **36**, 148-172, 1999.
6. Wicks DA, Wicks Jr. ZW, Multistep chemistry in thin films; the challenges of blocked isocyanates, *Prog Org Coat*, **43**, 131-140, 2001.
7. Ranjbar Z, Montazeri Sh, Nayini MMR, Jannesari A, Synthesis and characterization of diethylene glycol monobutyl ether-blocked diisocyanate crosslinkers, *Prog Org Coat*, **69**, 426-431, 2010.
8. Ishizu K, Makino M, Hatoyama N, Uchida S, Emulsion-induced ordered microporous films using amphiphilic poly(ethylene oxide)-block-poly(*n*-butyl isocyanate) block copolymers, *J Appl*

- Polym Sci*, **108**, 3753-3759, 2008.
9. Ji Y, Kim J, Bae JY, Flame-retardant ABS resins from novel phenyl isocyanate blocked novolac phenols and triphenyl phosphate, *J Appl Polym Sci*, **102**, 721-728, 2006.
  10. Wei WJ, Guo ZR, Zhang YF, Pan EL, Study on *N*-hydroxyphthalimide as blocking agent for isocyanates, *J Appl Polym Sci*, **84**, 1346-1352, 2002.
  11. Girones J, Pimenta MTB, Vilaseca F, Carvalho AJF, Mutje P, Curvelo AAS, Blocked diisocyanates as reactive coupling agents: application to pine fiber-polypropylene composites, *Carbohydr Polym*, **74**, 106-113, 2008.
  12. Girones J, Pimenta MTB, Vilaseca F, de Carvalho AJF, Mutje P, Curvelo AAS, Blocked isocyanates as coupling agents for cellulose-based composites, *Carbohydr Polym*, **68**, 537-543, 2007.
  13. Sankar G, Sultan Nasar A, Cure-reaction kinetics of amine-blocked polyisocyanates with alcohol using hot-stage Fourier transform infrared spectroscopy, *J Appl Polym Sci*, **109**, 1168-1176, 2008.
  14. Caille D, Pascault JP, Tighzert L, Reaction of a di-epoxide with a diisocyanate in bulk. II: Use of an imidazole or a blocked isocyanate catalysts, *Polym Bull*, **24**, 31-38, 1990.
  15. Moszner N, Zeuner F, Salz U, Rheinberger V, Reaction behaviour of monomeric/ $\beta$ -ketoesters. 3. Polymerizable reaction products of 2-acetoacetoxyethyl methacrylate with aromatic isocyanates and aldehydes, *Polym Bull*, **33**, 43-49, 1994.
  16. Viganò M, Levi M, Turri S, Chiari M, Damin F, New copolymers of *N,N*-dimethylacrylamide with blocked isocyanates for oligonucleotide immobilization in DNA microarray technology, *Polymer*, **48**, 4055-4062, 2007.
  17. Wicks DA, Yeske PE, Amine chemistries for isocyanate-based coatings, *Prog Org Coat*, **30**, 265-270, 1997.
  18. Ubaghs L, Keul H, Hocker H, Novel intramolecular blocked isocyanates as stable one-component systems for poly(urea urethane)s, *Polymer*, **46**, 1459-1465, 2005.
  19. Parker DK, Musleve RT, Process for the synthesis and recovery of tetrahydro-*N*-[1-methyl-1-[3-(1-methylethenyl)-phenyl]ethyl]-2-oxo-1-*H*-pyrrolo-1-carboxamide, *US Patent 5,208,347* (4 May 1993).
  20. Parker DK, Weinstein AH, Colvin HA, Crosslinkable rubber composition, *US Patent 5,043,455* (27 Aug 1991).
  21. Weinstein AH, Colvin HA, Parker DK, Crosslinkable rubber composition, *US Patent 4,983,684* (8 Jan 1991).
  22. Shanxi Provincial Institute of Chemical Industry, Isocyanate. In: *Polyurethane Elastomer (Chinese)*, Beijing, Chemical Industry, 624-633, 2001.
  23. Petrak S, Shadurka V, Binder WH, Cleavage of blocked isocyanates within amino-type resins: influence of metal catalysis on reaction pathways in model systems, *Prog Org Coat*, **66**, 296-305, 2009.
  24. Xu PL, Zhang SQ, Catalyst. In: *Handbook of Polyurethane Materials (Chinese)*, Beijing, Chemical Industry, 101-102, 2002.
  25. Song CM, Luo ZY, Chen X, Lu MX, Xiao RR, Blocking and unblocking reaction of PAPI, *Polyurethane Industry*, **15**, 9-13, 2000.
  26. Zhang HL, Yang X, Wang YS, Blocking reaction of PAPI with phenol, *Polyurethane Industry*, **20**, 25-27, 2005.

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عضویت در  
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مباحث پیشرفته یادگیری عمیق؛  
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