WaterdispersibleBlockedAromaticdiisocyanateIonomers

S.Subramani · Hyun-Chul Kong · In Woo Cheong · Jung-Hyun Kim
Nanosphere Process and Technology Laboratory, Department of Chemical
Engineering, Yonsei University, Seoul 120-749, Korea

수분산 Blocked Isocyanate 합성에 관한 연구

S.Subramani · 공현철 · 정인우 · 김종현
연세대학교 화학공학과 기능성 초미립자 공정연구실

Abstract
Making water dispersible/reducibleblocked-isocyanates facilitates incorporation of blocked
isocyanates into an aqueous dispersion of coreactant. Anionically modified methyl ethyl
ketoxime (MEKO), -caprolactam (CL) and 3,5-dimethylpyrazole (DMP) blocked aromatic
diisocyanates (TDI and MDI) dispersible isocyanate adducts were prepared by introducing
ionic pendant groups and characterized by FTIR, GPC, DSC and TGA techniques. It was
found that molecular weights of MDI-based polyisocyanates were higher. Thermal studies
showed that the de-blocking temperature of the isocyanate adducts decreases in the
order: -caprolactam > methyl ethyl ketoxime > 3,5-dimethylpyrazole. It was also found
that the dispersions of blocked adducts are stable and compatible with polyurethane
(polyether and polyester based) and acrylic dispersions.

Introduction
Polyurethanes are versatile polymers that contain the carbamate structure (-NH-CO-O-).
The high reactivity and toxicity of isocyanates do not allow their storage and use in
one-pack systems. Blocked isocyanates are a solution to overcome these drawbacks.
Blocked isocyanate is an adduct containing a comparatively weak bond formed by the
reaction between an isocyanate and a compound containing an active hydrogen atom. At
elevated temperatures the reaction tends to proceed in such a way as to regenerate the
isocyanate and blocking agent. The regenerated isocyanate can react with a substrate
containing the hydroxyl functional group to form thermally more stable bonds. The
dissociation or de-blocking temperature of the blocked isocyanates is one of the limiting
factors in industrial applications. The rate and extent of de-blocking reaction depend on
many factors: the structure of isocyanate and blocking agent including substituents,
solvents, catalysts, temperature and the thermal stability of the isocyanate-blocking
agent bond. The most widely used commercial blocking agents are phenols, oximes,
alcohols, -caprolactam, 3,5-dimethyl pyrazole and diethyl malonate.
Due to the extreme reactivity of aromatic isocyanates (MDI and TDI) towards water molecules, they are unsuitable for water-based polyurethane dispersion coatings. To eliminate such type of reaction with water, the isocyanates groups have to be protected by blocking with suitable blocking agents like -caprolactam, methyl ethyl ketoxime, phenol, triazoles, imidazoles, amines etc. In this paper it was reported that the preparation and properties of some water-reducible anionic blocked aromatic diisocyanates dispersions using aromatic diisocyanates (MDI and TDI), dimethylolpropionic acid (DMPA) and MEKO, DMP and - caprolactam as blocking agents.

**Experimental**

**Materials**

All these materials are laboratory grade chemicals and are used without any further purification.

**Synthesis of water reducible blocked isocyanate based ionomer adducts.**

A 500 ml 4-necked flask equipped with mechanical stirrer, nitrogen inlet, condenser was charged with dimethylol propionic acid (DMPA) and N-methyl pyrrolidone (NMP). The reactants were heated to 80°C in a constant temperature silicone oil bath. TDI was added to the reaction mixture and the reaction was carried out until theoretical NCO content was reached. Upon obtaining the theoretical NCO value, required quantity of blocking agent was added to the reaction mixture and the reaction was further carried out until no NCO peak could be detected in the IR spectrum. These blocked isocyanates were water reducible/dispersible after neutralization with base compound. The synthesis of MDI based adducts were carried out at 70°C.

**Characterizations**

FT-IR spectra for the anionic blocked diisocyanate adducts were recorded using Bruker Tensor 27 FTIR analyzer in the range of 400-4000 cm. Molecular weight (Mw and Mn) and Polydispersity were measured by gel permeation chromatography (GPC). Differential scanning calorimeter (DSC), TA Instruments Model DSC Q10 and Thermo-gravimetric analyzer, TA Instruments Model TGA Q50 was used to study the thermal properties. Adducts were washed with distilled water several times to remove NMP and neutralized with TEA. Finally, water was added to the neutralized adducts and taken for stability and miscibility studies.
Results and Discussion

Synthesis of water dispersible blocked isocyanate ionomer adducts
The reaction was carried out till disappearance of NCO absorption peak at around 2250-2270 cm⁻¹. This indicates complete blocking of NCO-groups by blocking agents.

GPC Analysis

The data showed that molecular weight (Mw and Mn) and polydispersity of MDI-based adducts were higher compared to TDI-based adducts. In the case of blocking agents, molecular weights of MEKO- and DMP-blocked adducts were lower than that of caprolactam-blocked ones except DMP-blocked MDI. This was well understandable from fast reactivity of MDI.

Thermal Properties

DSC curves of blocked adducts showed broad endotherm, which is due to the de-blocking of blocking agents. The broad de-blocking temperature range may be due to slow and controlled release of blocking agents. It was also understood that, for anionic blocked polyisocyanate samples, the melting of the short- and long-range order in hard segment domains of polyisocyanate might take place at these temperature ranges where unblocking might occur. This is another reason for the broadening of the DSC curve and affect the determination of the unblocking temperature range by DSC measurement. MEKO-blocked TDI adduct de-blocks at lower temperature (approximately in the range 70-150°C) than MDI adduct (approximately in the range 90-180°C). The same trend was observed in MEKO-TDI adduct (108°C) and MEKO-MDI adduct (120°C), which was reported in the literature. Caprolactam-blocked TDI and MDI adducts de-block at same temperature range (110-180°C). DMP-blocked MDI adduct de-blocks at 75-125°C. TGA curves of MEKO-blocked TDI and MDI adducts showed that these adducts dissociates at 130°C and 75°C, respectively. Caprolactam-blocked TDI and MDI adducts de-block at 120°C. DMP-TDI and DMP-MDI adducts undergoes decomposition at 75 and 105°C, respectively. In general, dissociation temperatures of blocked aromatic isocyanate are always lower than blocked aliphatic isocyanates. The de-blocking temperature of DMP, MEKO and caprolactam are found to be in the order: DMP < MEKO < Caprolactam.

Storage Stability

Generally surfactants are used to stabilize the dispersions of blocked polyisocyanate and polar solvents, such as N-methyl pyrrolidone were used as co-solvents. It was noticed that there was no gelation and setting of adducts in this period. This indicates that the storage stability of the dispersions is good and confirms no de-blocking. DMP and
MEKO-blocked adduct shows better miscibility than -caprolactam-blocked adducts due to the presence of the aliphatic substituent. Improvement in the solubility (miscibility) of blocked isocyanate using a methyl-substituted blocking agent has been reported. The low miscibility of -caprolactam-blocked adduct may be due to its cyclic structure and less polar nature after blocking reaction.

Conclusion

Water dispersible/reducible anionic methyl ethyl ketoxime, 3,5-dimethylpyrazole and -caprolactam blocked aromatic diisocyanate (TDI and MDI) dispersions were successfully prepared and characterized. Molecular weight of MDI-based adducts was higher compared to TDI-based adducts. The thermal studies of these adducts confirmed that the de-blocking temperature increase in the following order: 3,5-dimethyl pyrazole < methyl ethyl ketoxime < -caprolactam. Storage stability results showed that all dispersions prepared were stable for more than six months. The dispersions prepared all were in liquid form and miscible (compatible) with polyurethane dispersions (polyether and polyester based) and acrylic dispersion. These anionically modified blocked isocyanate adducts can be used as potential crosslinkers.

References