Catalysis of the Reaction between Isocyanates and Protonic Substrates. III. Influence of the Addition of a Cosolvent on the Polyurea Foaming Process
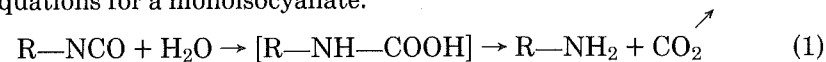
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Synopsis

Polyurea foams can be produced from nonmiscible water and polyisocyanates. The addition of a cosolvent improves the homogeneity of the reaction medium and enhances the effectiveness of any catalyst, preferably soluble in water. Cosolvents, exhibiting an intrinsic catalytic activity, display a regulating effect on the rise profile of the foams and allow for defining performant and less expensive formulations.

INTRODUCTION

Polyurea results from the reaction of a polyfunctional isocyanate with water. The reaction mechanism can be schematized by a two-step process, i.e., the following equations for a monoisocyanate:

$$R\text{—}NCO + H_2O \rightarrow [R\text{—}NH\text{—}COOH] \rightarrow R\text{—}NH_2 + CO_2 \nearrow \qquad (1)$$

$$R\text{—}NCO + R\text{—}NH_2 \rightarrow R\text{—}NH\text{—}CO\text{—}NH\text{—}R \qquad (2)$$

The carbon dioxide evolved acts such as the foaming agent, but good quality foams are only obtained when suitable catalysts such as amines[1,2] or metal salt–amine complexes[3] are used.

The reaction medium consists of two nonmiscible phases containing isocyanate or water, respectively. Another paper has shown the strong influence of the heterophase conditions on the course of the foaming process.[4] Indeed, the reaction takes place in the organic phase wherein the effective concentration of the catalyst is determined by its partition coefficient between organic and aqueous phases. Thus the polyurea production would be better controlled when the catalyst is entirely in the organic phase. This paper reports some results obtained in that prospect by adding a cosolvent into the reaction medium.

In the commonly used formulations, an excess of water (5- to 10-fold) is recommended to dissipate a part of the reaction heat and to control the temperature rise. Furthermore, *tris*-(2-chloroethyl)phosphate (TCEP) is added to improve the physical characteristics of the end products. It is virtually impossible to determine the partition coefficient of the catalyst between water and the isocyanate solution in TCEP. Indeed the polyurea formation starts immediately after the mixing of the two phases, and the temperature increases quickly. Only the partition coefficient of the catalyst between water and TCEP can be measured at constant temperature.[4] To improve the experimental conditions, enough

cosolvent can be added to catalyst, water, and TCEP to obtain a homogeneous medium. However, when isocyanate is added, the immediate formation of insoluble polyurea does not allow us to know whether the initially homogeneous liquid phase demixes or not.

Dimethylformamide (DMF), dioxane, and N-methyl 2-pyrrolidone (NMP) were separately used as cosolvent in formulations based on diphenylmethane 4,4'-diisocyanate (MDI).

EXPERIMENTAL

The amine catalysts were used as received from PRB-Recticel (Polyurethane Foam Division, Wetteren, Belgium). They are listed in Table I with their molecular structure. Dimethylformamide (Baker), dioxane (Baker), N-methyl 2-pyrrolidone (Aldrich), and TCEP (Hoechst) were used without any further purification. Crude diphenylmethane 4,4'-diisocyanate (Shell) contained 31.5 wt % of NCO groups.

The CO_2 evolution was monitored thanks to a device previously described.[3] Foaming was tested on a reduced scale by pouring the reactive formulation into a cubic brown-paper box (15 cm side) lined with a polyethylene foil.[3]

RESULTS AND DISCUSSION

Figures 1 and 2 show the influence of the addition of dioxane as cosolvent on the CO_2 evolution curves registered for different amine catalysts. In this series of measurements, the overall concentrations of MDI and each catalyst as well

TABLE I
The Amine Catalysts and Their Molecular Structure

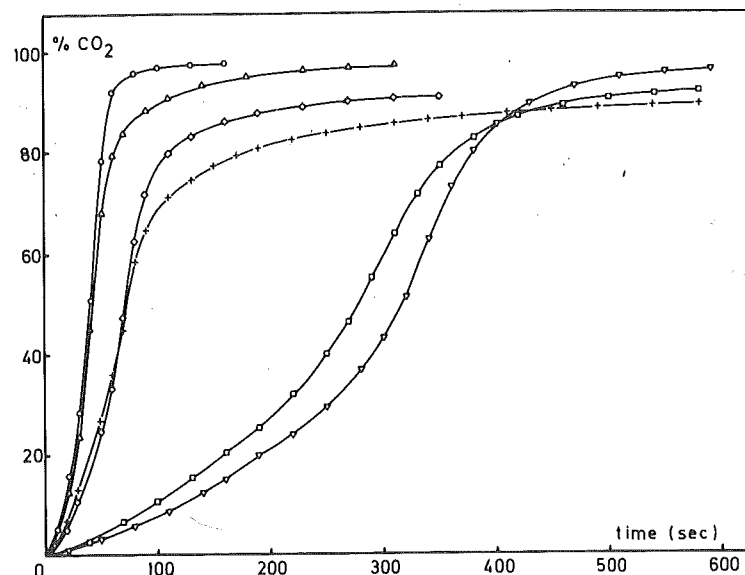| DABCO | Diazabicyclo [2,2,2]octane |
DB	N,N-dimethylbenzylamine
DMEA	2,2'-Oxy-bis(N,N-dimethylethylamine)
DMP	Tris-(N,N-dimethylaminomethyl)phenol
2MI	2-Methylimidazole
TMG	Tetramethylguanidine
NMP	N-methyl 2-pyrrolidone

Fig. 1. CO_2 evolution curves; effect of dioxane used as cosolvent. No dioxane added to 100 parts MDI, 54 parts H_2O and 75 parts TCEP: (+) TMG (1.5 parts); (□) 2MI (1.05 parts); (O) DMP (1.75 parts). 48 parts dioxane added to 100 parts MDI, 31 parts H_2O and 43 parts TCEP: (◇) TMG (1.5 parts); (▽) 2MI (1.05 parts); (△) DMP (1.75 parts).

as the TCEP over water volume ratio are kept constant. Whatever the one- or two-phase character of the reaction medium, the total volume is considered in the calculation of the so-called overall concentrations. In a two-phase system, the isocyanate (MDI) is completely in the organic phase wherein its effective
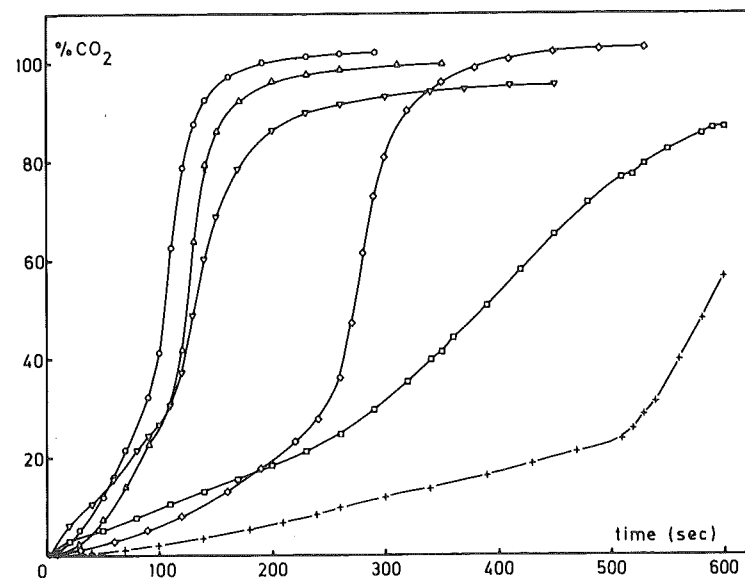

Fig. 2. CO_2 evolution curves; effect of dioxane used as cosolvent. No dioxane added to 100 parts MDI, 54 parts H_2O and 75 parts TCEP: (+) DABCO (1.5 parts); (□) DMEA (2.1 parts); (O) DB (3.45 parts). 48 parts dioxane added to 100 parts MDI, 31 parts H_2O and 43 parts TCEP: (◇) DABCO (1.5 parts); (▽) DMEA (2.1 parts); (△) DB (3.45 parts).
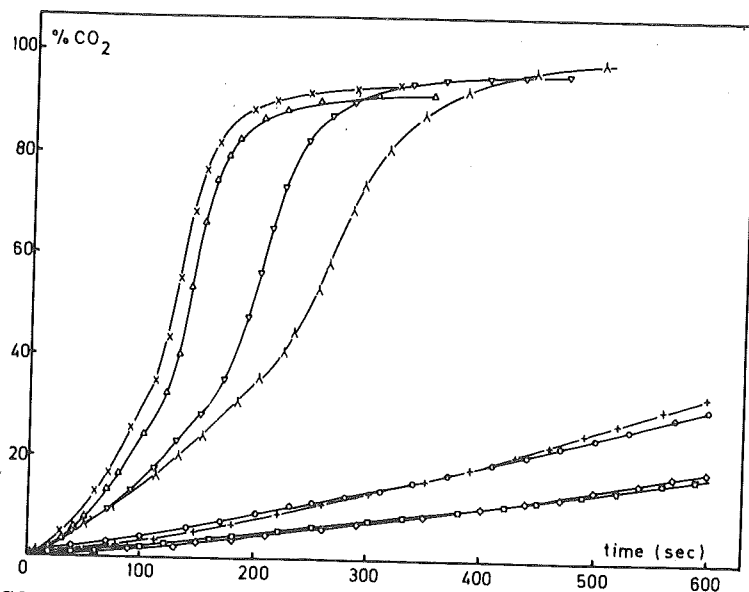
Fig. 3. CO_2 evolution curves; effect of DMF as cosolvent. No DMF added to 100 parts MDI, 48 parts H_2O and 67 parts TCEP: (+) 2MI (0.27 part); (□) DABCO (0.36 part); (○) DMEA (0.52 part); (◇) no catalyst. 33 parts DMF added to 100 parts MDI, 31 parts H_2O and 43 parts TCEP: (▽) 2MI (0.27 part); (△) DABCO (0.36 part); (X) DMEA (0.52 part); (λ) no catalyst.

Fig. 5. CO_2 evolution curves; intrinsic catalytic effect of NMP and dioxane in formulations based on 100 parts MDI and 0.21 part 2MI: (+) 31 parts NMP; (□) 20 parts NMP and 15 parts dioxane; (○) 10 parts NMP and 30 parts dioxane; (◇) 48 parts dioxane.

concentration is accordingly higher than the overall value. In a homogeneous reaction medium, overall and effective concentrations are equal.

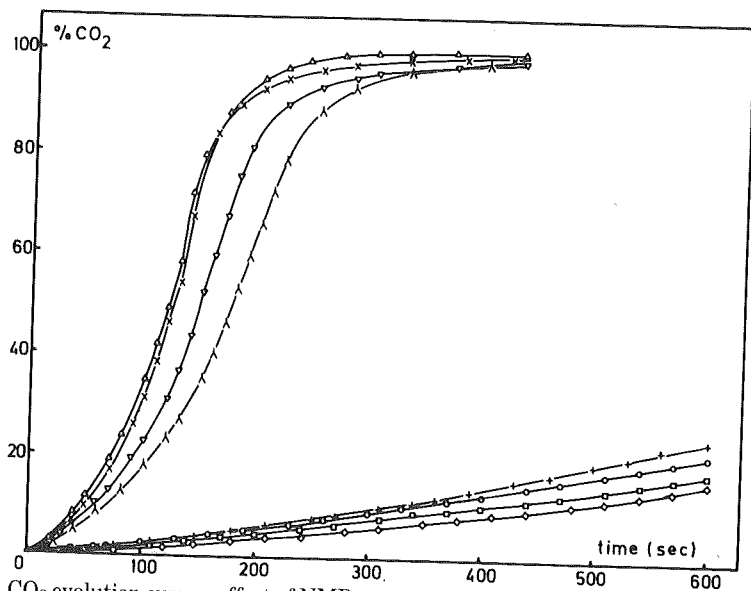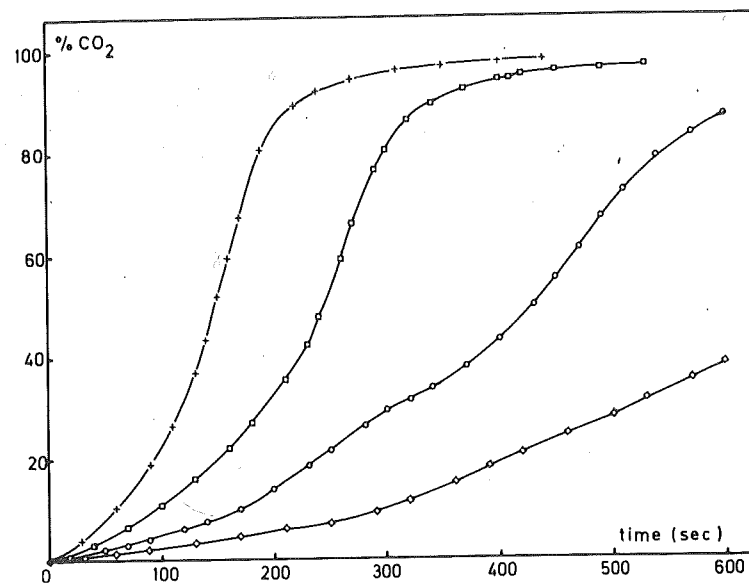From Figures 1 and 2, the activity of TMG, DMP, and 2MI is hardly affected

by the addition of dioxane. It is not surprising since all these protic catalysts react very easily with the polyfunctional isocyanate (MDI) and are therefore systematically present in the isocyanate-containing phase. The addition of dioxane seems to be responsible for a very slight decrease of the CO_2 evolution rate, mainly in the case of 2MI. This effect could be explained either by the dilution of the effective reaction medium resulting from the homogenizing effect,
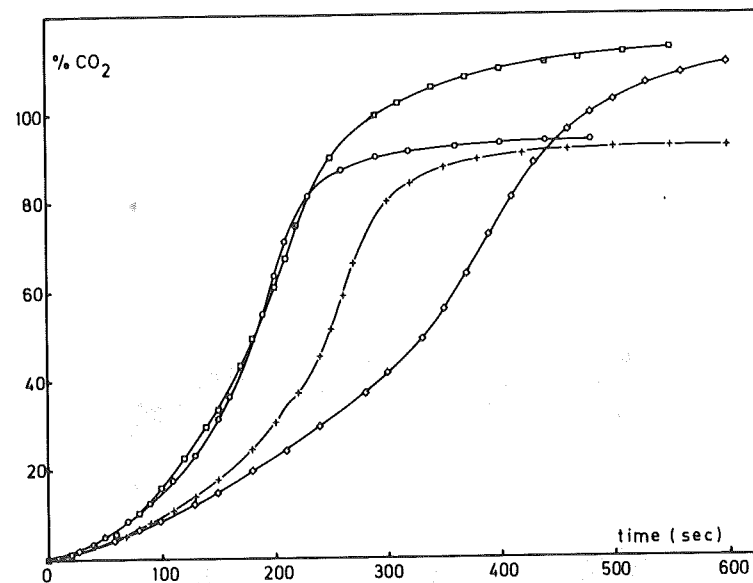

Fig. 4. CO_2 evolution curves; effect of NMP as cosolvent. No NMP added to 100 parts MDI, 46 parts H_2O and 64 parts TCEP: (+) 2MI (0.21 part); (□) DABCO (0.29 part); (○) DMEA (0.42 part); (◇) no catalyst. 31 parts NMP added to 100 parts MDI, 31 parts H_2O and 43 parts TCEP: (▽) 2MI (0.21 part); (△) DABCO (0.29 part); (X) DMEA (0.42 part); (λ) no catalyst.

Fig. 6. CO_2 evolution curves; effect of the TCEP/NMP ratio in formulations containing 100 parts MDI and 31 parts water. TCEP/NMP: (+) 1.7; (□) 1.1; (○) 1.4; (◇) 0.85.
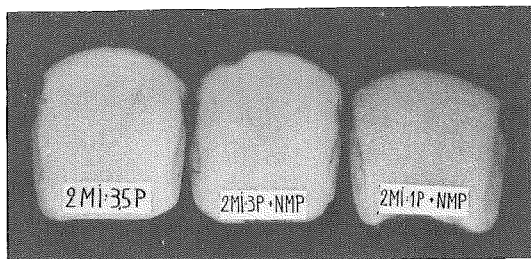
Fig. 7. Foams prepared from 2MI (3.5 parts); 2MI (3 parts) plus NMP, and 2MI (1 part) plus NMP, respectively.

or by a decrease of the dielectric constant influencing the kinetics of the isocyanate reaction with both water and the protic catalyst. As DB, DMEA, and DABCO are aprotic catalysts, they do not react with the isocyanate. The partition coefficient of DB between TCEP and water, at 25°C, is especially high (37) compared to the values determined for DMEA (0.145) and DABCO (0.015).[4] The favorable partition coefficient of DB toward the organic phase can explain why DB behaves very similarly to TMG, DMP, and 2MI. When DMEA and DABCO are used as catalysts, the polyurea foaming process is deeply modified by the addition of dioxane. The homogenizing effect of this solvent dramatically enhances the very low effective concentration of DMEA and DABCO in the isocyanate-containing phase. The improvement is so important that it largely outweighs the slight depressive effect observed for the other catalysts (mainly 2MI and DB).

Dimethylformamide (DMF) is a still more efficient cosolvent than dioxane, as it requires only 33.5 parts of DMF to homogenize 43 parts of TCEP and 31 parts of water, when 48 parts of dioxane are necessary. Figure 3 shows the beneficial effect of DMF on the CO_2 evolution curves recorded for DABCO, DMEA, and 2MI. Although the overall catalyst concentration is now approximately four times lower than before (Figs. 1 and 2), the CO_2 evolution rate remains quite high. Furthermore, the polyurea foaming process proceeds at a good rate even in the absence of any amine catalyst. That means, the cosolvent itself has a cocatalytic activity, which is in agreement with the observations of Briody and Narinesingh.[5]

The CO_2 evolution curves are representative of the foam rise profiles. When catalysts with a low effective activity in the heterophase reaction medium are used (DABCO, DMEA), DMF significantly improves the rise profile (Figs. 2 and 3), and the morphology and the quality of the end products also. Unfortunately,
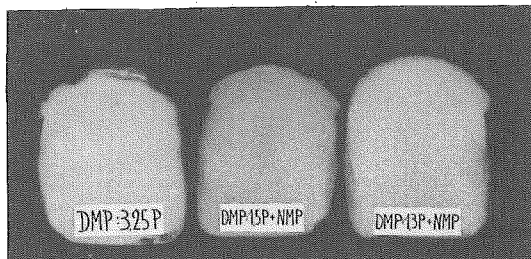

Fig. 8. Foams prepared from DMP (3.25 parts); DMP (1.5 parts) plus NMP, and DMP (1.3 parts) plus NMP, respectively.

DMF cannot be technically recommended because of its very unpleasant and persistant odor. It can, however, be advantageously replaced by N-methyl 2-pyrrolidone (NMP), which is, furthermore, a very safe solvent [high flash point: 204°F (95.6°C), good chemical and thermal stability].[6] Figure 4 ascertains the catalytic activity of NMP used as cosolvent. From Figures 3 and 4, it is obvious that NMP is cocatalytically more active than DMF, whereas it displays a more regular rise profile. NMP is also a little more efficient cosolvent to homogenize TCEP and water. The rise profile observed for the amine catalysts operating in the presence of NMP are again significantly improved. The high catalytic activity of NMP in the polyurea formation is convincingly established in a series of experiments wherein 2 MI is used as catalyst (Fig. 5). All the other conditions being kept constant, the system TCEP (43 parts) and water (31 parts) is made homogeneous by adding just enough dioxane, NMP, or various mixtures of these cosolvents, respectively. As the NMP proportion increases, the CO_2 evolution rate is drastically enhanced; this large effect cannot be explained by the slight decrease of the cosolvent volume (about 5% of the total volume).

All of the previous measurements (Figs. 1–5) were taken in a reactor, but in the presence of a defoaming agent. It is attractive to prepare polyurea foams on a reduced scale by taking advantage of the cosolvent effects. However, the formulations have to be adjusted to keep a sufficient viscosity of the foaming material in spite of the cosolvent addition, and to prevent any further collapse of the rising foam. This adjustment is delicate, as moderate changes in the formulation exhibit large effects on the CO_2 evolution curve monitored in the absence of amine catalysts; Figure 6 illustrates this phenomenon when the TCEP over NMP ratio is modified. Figures 7 and 8 show that the cosolvent NMP enables the preparation of very good polyurea foams with largely reduced amounts of amine catalysts. This procedure provides the producer with an attractive tool for controlling the cellular structure and the physicomechanical properties of the polyurea foams through proper adjustments of the TCEP, cosolvent, and catalyst balance.

In conclusion, the use of a cosolvent has a favorable effect on the catalysis of the polyurea formation as long as the catalysts are preferably soluble in water rather than in the MDI solution. Furthermore, when the cosolvent has its own catalytic activity, it displays a regulating effect on the rise profile of the polyurea foams. Finally, the use of a suitable cosolvent as NMP allows less expensive (±10%), although still performant, formulations.

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Pervaporation of Benzene–Cyclohexane Mixture by Poly(γ-methyl L-Glutamate) Membrane and Synergetic Effect of Their Mixture on Diffusion Rate

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Synopsis

The pervaporation of binary liquids mixture of benzene and cyclohexane was examined by use of poly(γ-methyl L-glutamate) (PMLG) membrane. The permeation rate–time curve for each of benzene and cyclohexane from their mixtures changed to the longer times side by increasing the cyclohexane in the mixtures. $t_{1/2}$ (the time required to reach a half-value of the steady state permeation rate) for the each component increased exponentially with increasing of cyclohexane, which has a smaller plasticizing effect on PMLG membrane than benzene, in the mixtures. The apparent diffusion coefficients, obtained from the steady state permeation and the sorption experiments, for benzene–PMLG and cyclohexane–PMLG are dependent exponentially on the sorbed amounts of benzene. This result was explained on the bases that the diffusion of cyclohexane was enhanced synergetically with benzene coexisting in the system. This effect influenced negatively the separation of the liquids mixture by pervaporation.

INTRODUCTION

Both benzene and cyclohexane are composed of the six-member rings of aromatic and aliphatic compounds, respectively, and are nonpolar ones. Since the difference of the temperature of boiling points between them is only 0.6°C and the interaction parameter between them is small, the liquid–vapor equilibrium curve of the binary liquids mixture is nearly a close-boiling system, and shows an azeotropic point at 61 mol % of benzene. However, different affinities between these solvents to polymers have been observed. Thus the separation of their mixture by distillation may be difficult, and the separation by use of permselectivity of polymer membrane was examined by some workers.[1–3]

Huang and Lin[1] showed an existence of maximum permeation rate of their mixture through poly ethylene membrane at a composition of 50% in feed. McCandless et al.[2] examined the separation of them by poly(vinylidene fluoride) membrane, and obtained a value of separation factor as 20. They added the solvent, such as dimethyl sulfoxide or dimethyl form amide, in the feed mixture to make the permeation rate increase. But the value of separation factor decreased to 6 by adding the solvent. Cabasso et al.[3] examined the separation and diffusion mechanism of them through polymeric alloy membranes of various composition of polyphosphonates and acetyl cellulose by using the techniques of sorption, desorption, permeation, and self-diffusion of benzene labelled C^{14}. They obtained the value of separation factor of about 13, and showed that the diffusion coefficients for benzene depended strongly on its concentration in the polymer and that the diffusion coefficients for mixtures depended on the diffusion time in the sorption experiments.