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Acrylated polyurethanes by reactive extrusion

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ABSTRACT

A one-step acrylated polyurethanes prepolymers synthesis by reactive extrusion and bulk reaction is discussed.

These oligomers are obtained by a simultaneous reaction of MDI, polycaprolactone and hydroxyethyl-acrylate. In order to obtain a high reaction conversion within the extruder, tin laurate catalyst was used at 90°C. In these conditions, an appropriate radical initiator can be introduced during the extrusion without double bond polymerization .Comparing bulk and reactive extrusion prepared products, oligomer Tg were respectively -18°C and +8°C for oligomers and +18°C and +27°C for the issued networks.

INTRODUCTION

Polyurethane acrylates (PUA) are increasingly populare combining intrinsic polyurethane and acrylate properties to the ease of application and ecological aspect of solventless use prepolymers.

Through the nature and stoechiometry of reactants, the structure of PUA and of the issued cross-linked polymer can easily be tailored to an important variety of applications[1]. PUA are used as adhesives, coating materials,[2] optical fiber coating[3], to prepare prepregs for high-strength composites.[4]

A two steps procedure is generally used for PUA synthesis. Typically, a diisocyanate is sequentially reacted with a stoichiometric quantity of a dialcohol and, in a second step,with an hydroxy terminated acrylate,[2] like hydroxy ethyl acrylate (HEA). An inverse synthesis can also be used. The diisocyanate is first reacted with the monoalcohol and secondly with a dialcohol.[3]

This paper deals with one step comparative synthesis of PUA in a batch reactor or in a co-rotating twin-screw extruder.

One advantage of the synthesis in the twin-screw extruder is the possibility of introducing additives, like fillers,during the continuous process of the PVA synthesis. The use of a twin-screw extruder as a bulk reactor means certain requirements, and some of the difficulties to overcome are, in our case, the reduced residence time of reactants in the extruder, and the reaction exothermal control. We generally work[5] with an average residence time tn less than 5 min. In this process, reaction temperature must be quite low and the radical initiator must be chosen in order to avoid radical polymerization of the acrylate double bonds during extrusion. Residual isocyoanate in the prepared product brings on a damaging evolution and, so as to have a high conversion at moderate temperature in a reduced time, reactoin must be catalyzed.

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EXPERIMENTAL

Materials

Liquid MDI was used in this study (CARADATE-30). The isocyanate index is E = 134.5 g/Eq (NFT52132). Polycaprolactone (PCL) is CAPA203 from SOLVAY. $\overline{M_n}$ = 400 g. mol-1. Functionnality = 2. Other reactants, HEA and initiators are ALDRICH. All reactants were used without further purification.

Apparatus

A Nicolet MX-1 specptrometer was used for FT-IR analysis. The isocyanate band at 2467 cm^{-1} was determined by the baseline technique.

A Mettler TA3000 was used for DSC at a 7.5°C.min^{-1} heating rate, under argon atmosphere.

Size exclusion chromatography (SEC) was performed in a Waters device equipped with UV and refractive index detectors. The solvent was THF at a 1.5 mL/min flow rate and a pressure of 5 x 10^6 Pa. Columns of PL (Polymer Laboratories) gel 1000 Å, 500 Å, 100 Å, 100 Å were used.

Number and weight average molecular weights were calculated using a calibration with polystyrene standards.

Reactive extrusion experiments were performed using a CLEXTRAL BC21 modular co-rotating twin-screw extruder. The screw diameter was 25 mm and the barrel length was 900 mm.

RESULTS AND DISCUSSION

Classical synthesis in bulk

- *Control of the alcohol-isocyanate reaction*. This system involves a competitive reaction of a monoalcohol and a dialcohol with a diisocyanate(MDI). The monoalcohol(HEA), acts as a chain ending agent, the dialcohol, polycaprolactone (PCL) acting as a chain extender, diol/MDI ratio controls the molar mass of the product. The stoichiometric ratio, [OH]/[NCO] = 1 is respected so as to avoid residual NCO or OH groups, but an excess of HEA is also possible. In a typical reaction, we use 1 equivalent HEA, 1 equivalent PCL, 2 equivalent MDI and 0.1 % hydroquinone. FT-IR was used to monitor the extent of the reaction in PUA synthesis using isocyanate absorbtion at 2390 cm-1 (ISO) and the PCL carbonyl at 1727 cm-1. After a 16 h reaction at room temperature and in bulk, the product is analyzed by DSC (Fig. 1). It presents one Tg at - 18°C. The exothermic peak at high temperature (90-210°C) is mainly attributed to double bond radical polymerization. At a higher temperature, polymer degradation is observed. The SEC chromatogram of this product.(Figure 2) shows residual HEA (27.9 min). The second peak at 26 min is attributed to HEA-MDI adduct. This product presents a long polydispersity I_p = 8.5. Even for a long reaction time, the conversion, at room temperature, is not total. In order to complete this reaction, a higher temperature and a catalyst, Tin dibutyl dilaurate is used. It is important to note that 0.5 % catalyst must be used at 80°C so that to obtain a reasonable conversion.in 5 min.

In order to carry out the reaction in an extruder, the choice of reactant must be made taking into account the fact that a clear separation must occur between polycondensation and the radical double bound polymerization. DSC is an appropriate tool for the control of such reactions. DSC run were performed with a rate of 7.5 K.min^{-1}. 0.3 % of different initiators were used. We note that for benzoyl peroxide and tert-butyl peroxybenzoate, the two reactions occur at the same time. Using AIBN, the two reactions are slightly separated. Only with the use of ditbu-peroxide, the two reactions are separated. The addition of 0.3 % of Tin dibutyl dilaurate accelerates the polycondensation reactions and, in this case, the two reactions are clearly separated (Figure. 3).

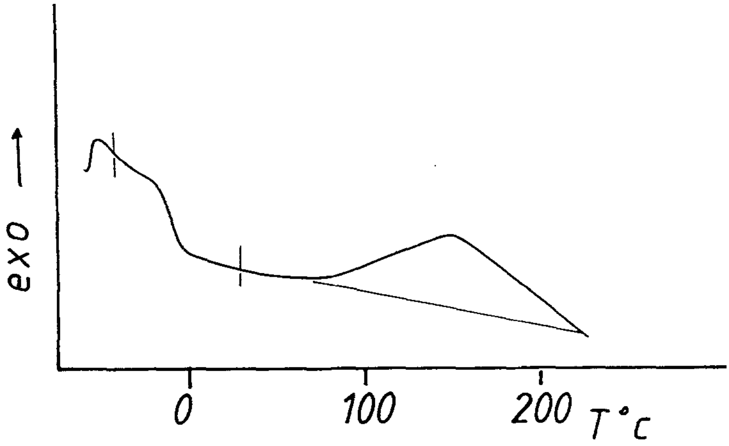

Figure 1 DSC thermogram of a PUA prepared at room temperature

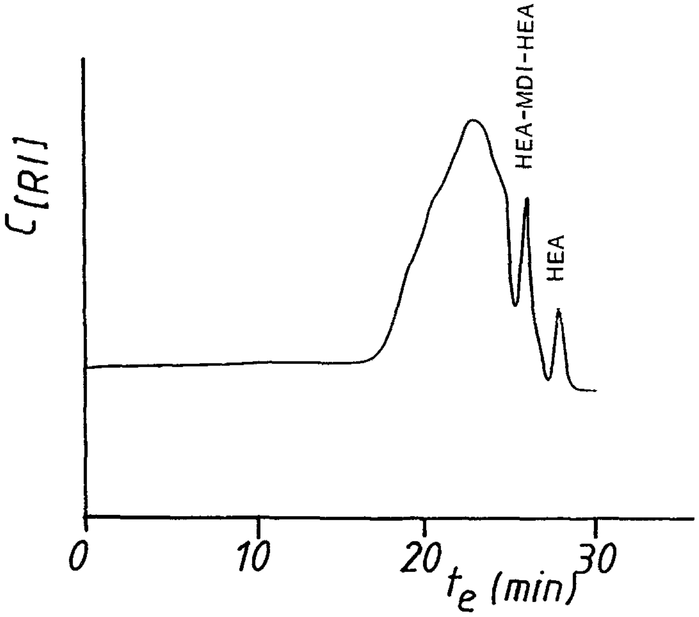

Figure 2 SEC chromatogram of a PUA prepared at room temperature

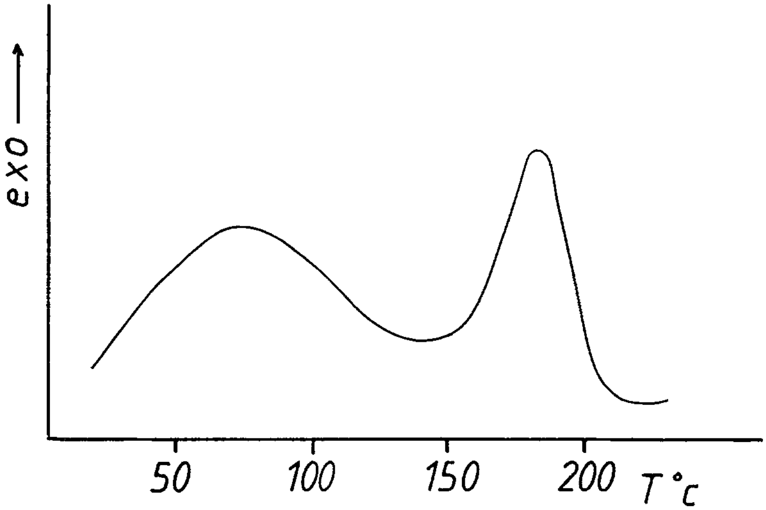

Figure 3 DSC thermogram of a PCL-HEA-MDI reaction. 0.3 % tin dibutyl-dilaurate and 0.3% tertiobutyl peroxide are used. Heating rate is 7.5°C.min^{-1}

Synthesis by reactive extrusion

It appeared that the following conditions are suitable to provide a reasonable degree of conversion within the extruder and, at the same time to avoid double bond radical polymerization and thus system reticulation during processing. 0.5 % tin dibutyl-dilaurate is to be used as a PU synthesis catalyst and 0.3 % dibutyl peroxide is to be introduced so as to prepare the acrylate functions polymerization . The maximum reaction temperature is 90°C. We choose a screw profile across the extruder containing 4 kneading disk areas, one of them continued by one element with a reveased pitch. This profile provides effective mixing and shearing thus preventing inhomogeneities formation during the process and a suitable residence time for this reaction (Figure. 4).

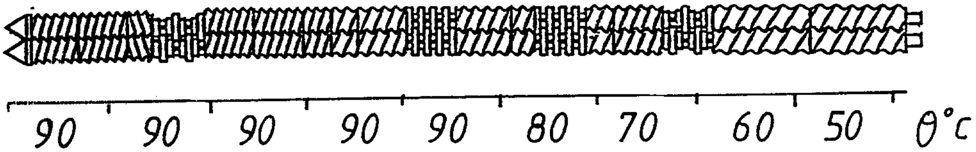

Figure 4 Screw profile used in PUA reactive extrusion

A mixture of PCL, HEA, catalyst is prepared and pumped through one side of barrel 1, MDI is pumped through the other side of the same barrel. We operate at 250 rpm and 2250 g.h^{-1} input. The radical initiator was introduced through barrel 9 for the second part of the experiment.

During extrusion, the product temperature was measured at different points. We did not observe any significant overheating effect, and the product temperature, at the extruder nozzle was 90 ± 2°C.

Residence time distribution (RTD) is an important reaction parameter and must be analyzed for a comprehensive reactive extrusion process. Diphenyl was used as a UV tracer for RTD determination. Diphenyl was injected as an impulse in the feed hopper into the extruder. Samples were collected from the extruder die diluted in THF and analyzed by SEC with an UV detector at 254 nm. The tracer concentration at time t (C_t) was calculated using a calibration curve.[5]

Having obtained C_t, we can calculate the extruder response to the inlet pulse (Et), the cumulative distribution (F_t), the mean residence time $\overline{t_n}$ and the variance σ_t^2 using the following equations :

$$E_t = \frac{Ct}{\sum_{0}^{\infty} C_t.\Delta T} \qquad \text{(eq. 1)}$$

$$F_t = \sum_{0}^{t} E_t.\Delta T \qquad \text{(eq. 2)}$$

$$t_n = \sum_{0}^{\infty} t.E_t.\Delta t = 223 \text{ sec} \qquad \text{(eq. 3)}$$

$$\sigma^2 = \sum_{0}^{\infty} (t-t_n)^2 . E_t.\Delta t = 138 \text{ sec} \qquad \text{(eq. 4)}$$

E_t and F_t are shown in Figure 5 .

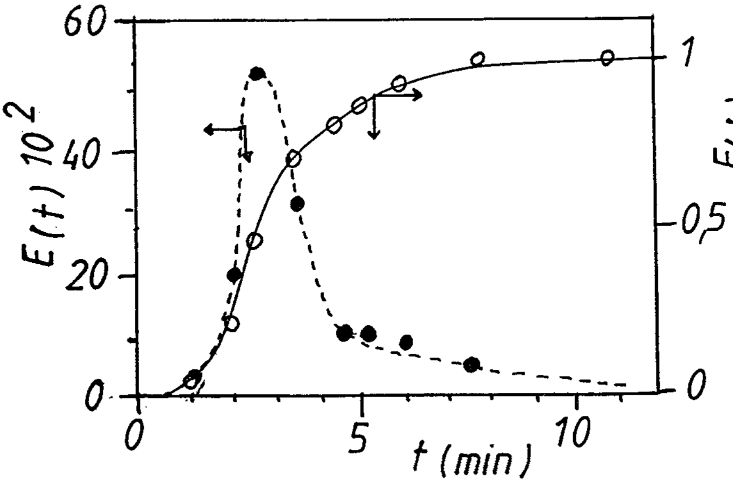

Figure 5 Residence time distribution during PC-HEA-MDI reactive extrusion

Samples were taken from the extruder die and occurately frozen in liquid nitrogen so that the product evolution is immediatly stopped. Products were analyzed using FT-IR, DSC and SEC (Fig. 6, Table I)

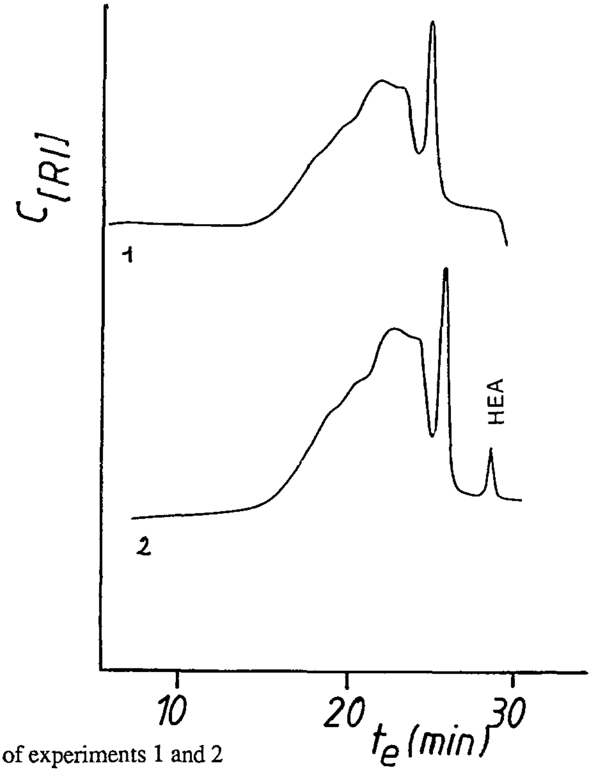

Figure 6 SEC of experiments 1 and 2

Table I

Prepolymer	Classical synthesis in bulk	Synthesis is twin-screw extruder Exp. (1)	Exp. (2)
P % (FT-IR	86	99.6	88
Tg (°) Prepolymer	- 18	8	7
$\overline{M_n}$ (PS) g.mol^{-1}	2800	3300	2300
Tg °C after cure	18	28	26

In the first part of the experiment, an almost total isocyanate conversion is observed. The addition of initiator induced a conversion decrease. This is probably due to a viscosity evolution inducing a flow change within the extruder and reducing t_n.

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