Analytical Investigations on Acrylic Polyurethane Hybrid-Dispersions

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Water-dispersible polyurethane acrylic graft copolymers are an important class of hybrid polymers for use as resins in waterborne coatings. In order to study fundamental properties of such polymers, a model system of four polyurethane macromonomers that differ in the average number of double bonds per molecule was developed. Free radical copolymerization of the polyurethane macromonomers with acrylates was carried out in aqueous phase using the polyurethanes as the reactive emulsifier. The stability of the product dispersions depends on the average number of double bonds per macromolecule and the weight ratio of hydrophilic polyurethane to the acrylic part. The content of the polyurethane double bonds and their conversion was measured by nuclear magnetic resonance (NMR) spectroscopy and by a titrimetrical method.

INTRODUCTION

Due to a growing interest in environmental compatible coating systems and rising limitations in the use of volatile organic compounds by law, waterborne coatings are becoming more important as alternatives to solventborne coatings. Since the beginning of the 1990s, a number of patents[1-18] have been published describing dispersions of polyurethane acrylic graft copolymers. The aim of formulating such hybrid dispersions is to combine the advantages of acrylics, such as gloss, hardness, and good affinity to pigments with the advantages of polyurethanes, such as chemical resistance and excellent mechanical properties.[19] By chemically binding the polyacrylate to the polyurethane via graft copolymerization, thermodynamical incompatibilities between the two polymer classes are overcome and the stability of the dispersions is increased. Usually the synthesis is carried out by preparing a polyurethane macromonomer containing polymerizible double bonds and copolymerizing it with acrylic monomers. There are two strategies to create an appropriate polyurethane macromonomer. One is to react an isocyanate prepolymer with a hydroxy group containing vinyl compound, e.g., 2-hydroxy ethyl acrylate, to form a polyurethane with terminal double bonds.[3,13] The alternative is to build in the polymerizible groups laterally using suitable dihydroxy functional compounds such as trimethylolpropane monoallylether in the polyaddition process.[1]

To form stable aqueous dispersions, either the polyurethane or the acrylic part has to contain hydrophilic groups. The most common way described in patent literature is to create amphiphilic polyurethanes consisting of polyester segments and hydrophilic compounds. Mostly sulfonic or carboxylic acid groups are used for hydrophilation,[1,12-13] which are neutralized to anions before dispersing. A widely applied component is dimethylol propanoic acid (DMPA), which has some advantage because of the very low reactivity of its acid group against isocyanates. This can be explained by steric hindrance effects.[20] There are also patents describing hybrid dispersions with nonionic polyurethanes. In these cases, stabilization of the dispersions is achieved by building hydrophilic polyether segments into the urethane.[4]

Radical copolymerization with acrylates can either be carried out in organic phase[2] or in aqueous phase.[1] In the first case, the final hybrid product is dispersed into water afterwards. The more preferred method uses an aqueous polyurethane dispersion as emulsifier to carry out radical copolymerization in this dispersion.

Many different composition variations of the educt monomers, for both the polyurethane and the acrylic part, can be taken from patent literature; but only a few fundamental basic investigations on the composition and properties of final products have been published.[21,22]

The aim of the present work is to investigate the chemical composition of the final products and how experimen-

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Table 1—Composition of the Polyurethane Macromonomers

Monomers	PUR-0	PUR-1	PUR-2	PUR-4
TMP-MA	—	150.9 g	277.9 g	383.0 g
IPDI	136.8 g	385.0 g	531.8 g	621.3 g
NPG	42.7 g	—	—	—
DBTL	0.1%	0.1%	0.1%	0.1%
MIBK	176.5 g	705.9 g	705.9 g	564.7 g
MPEG-2000	820.5 g	3464.1 g	3190.2 g	2203.7 g

tal condition changes affect this composition. Questions to be answered are whether or not grafting on the double bonds of the polyurethane macromonomer is taking place and which part of these double bonds is reacting under the chosen conditions. Furthermore, it has to be determined if the macromonomer can homopolymerize and whether a part of acrylic homopolymer is formed in the final product. If a polyurethane molecule contains more than one polymerizable double bond, the molecule might act as a crosslinking agent to form a network during copolymerization with acrylate.

For our investigations, we chose a model system of four different polyurethane macromonomers with allylic double bonds, built in laterally via trimethylolpropane monoallylether. The average content of double bonds per molecule was one (PUR-1), two (PUR-2), and four (PUR-4), respectively. In addition, a polyurethane without any double bond (PUR-0) was prepared substituting trimethylolpropane monoallylether with neopentyl glycol. Hydrophilation of the polyurethanes was achieved by introducing polyether segments in the polymer backbone. For every polyurethane macromonomer, three copolymerizations with acrylates were carried out in aqueous phase, changing the mass ratio of polyurethane to acrylate.

EXPERIMENTAL

Synthesis of Polyurethane Macromonomers

A five-liter steel reactor was charged with isophorone diisocyanate (IPDI), trimethylolpropane monoallylether (TMP-MA) and methyl isobutyl ketone (MIBK). The reaction mixture was stirred and heated to 80°C under nitrogen atmosphere. Dibutyl tin dilaurate (DBTL) was added as a catalyst and the reaction was carried out until a prepolymer with a constant isocyanate value was formed. Then, methoxy polyethylene glycol (M_n = 2000 g/mol) was added. The polyether was dried before use by azeotrop distillation with 5% cyclohexane to remove traces of water. In the case of polyurethane PUR-0, neopentyl glycol (NPG) was used instead of TMP-MA. The reaction was carried out until no residual isocyanate groups were detectable. The amounts of the different monomers used are shown in *Table* 1.

Dispersion of the Polyurethane Macromonomers

After total conversion, the polymers were dispersed in water using the acetone procedure.[23] Demineralized water was added to the dissolved polyurethanes via a dropping funnel at 50-60°C. After addition, MIBK was removed under reduced pressure. The solid phase content was adjusted to 40% by mass.

Free Radical Copolymerization of the Polyurethanes

A five-liter steel reactor was charged with the polyurethane macromonomer dispersions (PUR-0, PUR-1, PUR-2, and PUR-4, respectively) and kept under nitrogen. The dispersions were diluted with water so that the solid phase content of the reaction products was 40% by mass. After heating the reaction mixture to 80°C, a mixture of different acrylate monomers and a solution of tert-butyl peroxy ethyl hexanoate (TBPEH) in 10 ml MIBK were added over a period of four hours via dropping funnels. The acrylate mixture consisted of 20% styrene, 30% 2-hydroxy ethyl acrylate, 25% methyl methacrylate, and 25% n-butyl acrylate.

The total amount of initiator for each polymerization was 5% TBPEH based on the mass of the acrylate mixture. The mass ratio of polyurethane to acrylate was varied for each macromonomer as 1:1, 1:0.5 and 1:0.25.

NMR Measurements

Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on a Varian Unity 400 at 400 MHz. For quantitative measurements, dimethyl terephthalate was used as internal standard.

Titration of Double Bonds

All titrations were carried out potentiometrically with an automatic titrator (Mettler Toledo DL53) using a Pt/Ag/AgCl electrode (Mettler Toledo DM 140 SC). The following procedure was applied for soluble samples:

The sample was weighed into a flask and dissolved in 10 ml chloroform. The sample amount was based on the content of double bonds; between 0.15 and 0.27 mmol double bonds were charged. Then 5 ml of iodine monobromide solution were added [11 g IBr in 500 ml acetic acid (100%)] and allowed to react for two hours. The unreacted excess of IBr was then turned into an equivalent amount of iodine by adding 10 ml of potassium iodide solution (10 g KI in 100 ml demineralized water). Determination of the formed iodine was carried out by titration with sodium thiosulphate (c = 0.1 mol/l) under vigorous stirring.

Changes for insoluble gel samples: The samples were first swollen for one hour in 20 ml chloroform before

Table 2—Stability of the Product Dispersions

Mass Ratio Polyurethane: Acrylate	PUR-1	PUR-2	PUR-4	PUR-0
1 : 1	Unstable	Stable	Stable	Unstable
1 : 0.5	Stable	Stable	Stable	Unstable
1 : 0.25	Stable	Stable	Stable	—

adding the IBr solution. To avoid wall fouling on the flask during titration, 2 g sea sand were added.

Blank tests without any polymer were measured in the same manner.

RESULTS AND DISCUSSION

Stability of the Product Dispersions

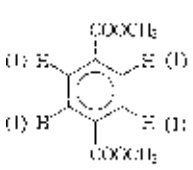
All polyurethane macromonomers were readily dispersible in water and formed stable systems. Graft copolymerization with the acrylate mixture led to coagulation when the mass ratio of acrylate to polyurethane was too high. The product dispersion of PUR-1 with a mass ratio of polyurethane to polyacrylate of 1:1 was not stable, in contrast to the product of the same polyurethane where the mass of the acrylic part was only half that of the polyurethane. At constant mass ratio, the stability of the product dispersion depends on the content of double bonds in the macromonomers. At a ratio of 1:1, no stable products result from grafting on PUR-0 and PUR-1, while the hybrid dispersions of PUR-2 and PUR-4 had excellent stability over months. The dispersion stability of all copolymer products is shown in *Table* 2.

This stability behavior can be understood by assuming a better stability of dispersions where the hydrophobic acrylic part is grafted onto the hydrophilic polyurethane. The more double bonds a polyurethane contains per molecule, the higher the probability of successful grafting.

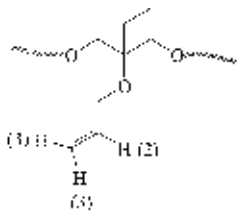
Determination of Polyurethane Double Bonds

The amount of allylic double bonds in the polyurethane macromonomers was determined using NMR spectroscopy and an alternative tritrimetrical method. NMR signals due to the allylic double bonds can be clearly observed (*Figure* 1). As an internal standard, a defined amount of dimethyl terephthalate was added to each sample.

The signal (1) at 8,1 ppm is assigned to the protons of the aromatic ring of the standard. Signals (2) and (3) are caused by the protons of the allylic groups in the polyurethane macromonomer.



dimethyl terephthalate



allylic double bond of macromonomer

Because there are not any other signals in the chemical shift region of the allylic protons, no interference occurs. Therefore, the content of double bonds (mmol per gram polymer) can be calculated from the ratio of the integrals of peak (1) to peak (2) or (3), respectively.

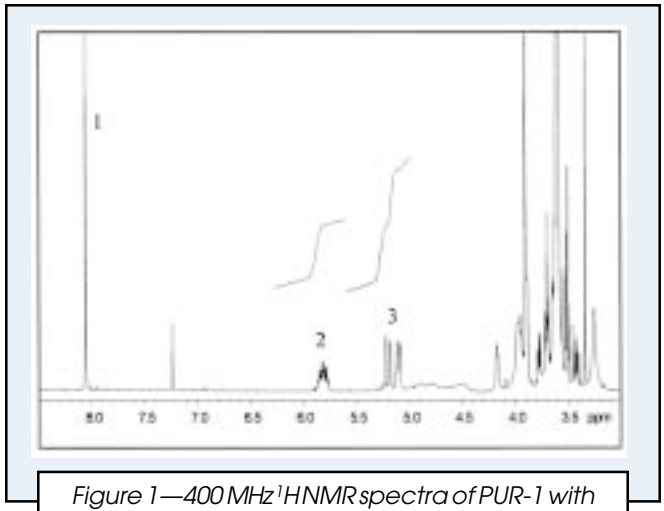


Figure 1—400 MHz ^{1}H NMR spectra of PUR-1 with dimethyl terephthalate as internal standard.

The results determined by NMR spectroscopy agree well with the values measured by iodometric titration as shown in *Table* 3.

The iodometric titration we used proved to be best suitable for quantitative determination of the polyurethane double bonds. This method is based on a well established method for fatty acid analysis.[24] It uses the addition reaction of iodine monobromide to the double bonds. After complete addition, an unreacted excess of this reagent is turned into an equivalent amount of iodine by adding potassium iodide. This iodine equivalent can be determined by iodometric titration. An exact and highly reproducible determination of double bond content is possible by optimizing the titration conditions. In addition, it is a selective method because only double bonds with a sufficiently high electron density are detectable. For example, acrylate monomers do not react because of the electron deficit of their double bonds.

After successful graft copolymerization, the content of allylic double bonds in the product samples should decrease significantly. For any comparison between the contents of double bonds of the hybrid products and the adduct macromonomers, the dilution of the samples with acrylate has to be taken into account when calculating the conversion of macromonomer double bonds.

As some of the acrylated samples contained a small part of insoluble gel particles, the NMR spectroscopy was not applicable to determine the content of double bonds, due to extreme line broadening. In contrast, the titrimetrical method proved to be best suited for those samples. Time dependant diffusion experiments showed that reproduc-

Table 3—Content of Allylic Double Bonds of the Macromonomers. NMR, Titration, and Theoretical Values

Sample	NMR-Method mmol/g	Titration-Method mmol/g	Theoretical mmol/g
PUR-0	0.00	0.00	0.00
PUR-1	0.188	0.186	0.217
PUR-2	0.385	0.357	0.399
PUR-4	0.642	0.641	0.689

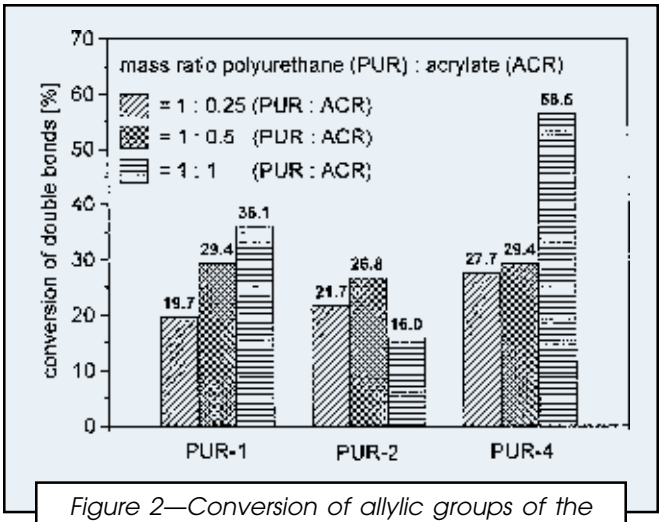


Figure 2—Conversion of allylic groups of the macromonomers PUR-1, PUR-2 and PUR-4 after graft copolymerization with different mass ratios of polyurethane macromonomer to acrylate.

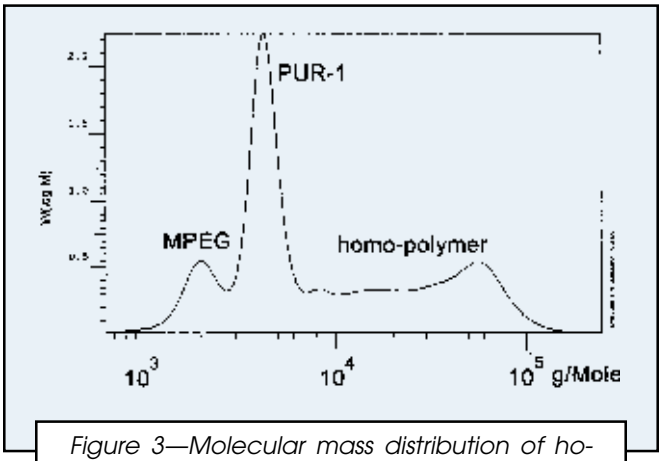


Figure 3—Molecular mass distribution of homopolymer of PUR-1.

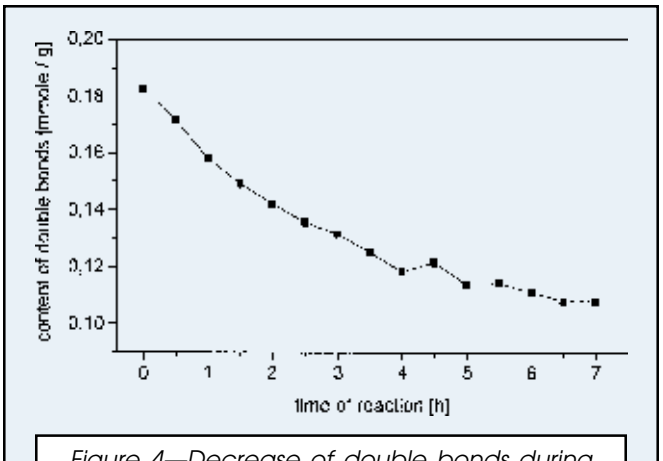


Figure 4—Decrease of double bonds during homopolymerization of PUR-1.

ible results can be obtained from this method. The iodine monobromide is able to migrate into the swollen gel particles and react with pendant double bonds inside the gel. In addition, we could rule out the possibility of a reaction between iodine monobromide and unreacted residual acrylate monomers that could lead to errors. In *Figure* 2, the conversion of the allylic macromonomer groups determined by titration is displayed.

It was observed that only a part of the allylic groups reacted during radical copolymerization. If we consider the polyurethanes to be chemically homogenous, which is certainly not true in reality, a conversion of 20% of PUR-1 means that only every fifth molecule reacts in statistical average. In contrast, a conversion of 50% of PUR-4 points out that, on average, each molecule has reacted twice. This may explain the excellent stability of the hybrid dispersions with high acrylic content formed with PUR-4 compared to the poor stability of the analogous PUR-1 hybrid dispersion.

Within an experimental series, the conversion of the polyurethane double bonds increases with higher acrylate content. An exception is the copolymer product of PUR-2 with the mass ratio 1:1, which can be explained because the significant part of insoluble gel particles was formed during this copolymerization. A possible explanation is that there are unreacted double bonds within these gel particles that are not accessible to radical polymerization.

The conversion of the acrylic monomers was determined by gas chromatography. Final conversions are between 96 and 98%.

Different efforts were made to investigate which part of the acrylic monomers was converted to graft versus homopolymer. Selective extraction of the final product using different solvent mixtures failed. It was also not possible to quantitatively separate the product by chromatographic methods (SEC/HPLC). Size exclusion chromatograms show a broad bimodal distribution of high molecular weight product beside a peak of residual ungrafted macromonomer. This bimodal distribution of the high molecular weight product indicates a mixture of graft and homopolymer.

Homopolymerization of Polyurethane Macromonomers

It is necessary to mention that a decrease in the content of macromonomer double bonds does not prove a successful acrylic grafting because of the possibility of homopolymerization of the macromonomers. Although a homopolymerization of these allylic compounds should not be favored due to degredative chain transfer, this possibility was examined by treating a PUR-1 dispersion with initiator in the absence of acrylates.

Surprisingly, GPC measurements of the product that was formed during seven hours of polymerization in batch show the formation of a significantly higher molecular mass species beside a peak of the residual macromonomer adduct (*Figure* 3).

In addition, the content of double bonds was observed over the reaction time by iodometric titration. The consid-

erable decrease in number fraction of double bonds indicates that these double bonds are involved in a chemical reaction. Measurements of the product revealed a final conversion of double bonds of 41% (*Figure* 4). However, titration results indicate that double bonds are consumed in a chemical reaction and no further information about the type of reaction can be extracted. However, if the experimental findings from both titration and GPC are considered, it is obvious that this reaction must have been a polymerization.

SUMMARY

In order to investigate fundamental aspects of acrylic polyurethane hybrid dispersions, a model system of four different polyurethane macromonomers was synthesized. These macromonomers differ in their average content of allylic double bonds, which were built in laterally via trimethylolpropane monoallylether. Free radical graft copolymerization of the polyurethane macromonomers with acrylates was carried out in aqueous phase. The stability of the final hybrid dispersions depends on both the average content of double bonds in the polyurethanes and the mass ratio of polyurethane to polyacrylate. Too much polyacrylate, together with a low double bond content of the polyurethanes, led to unstable product dispersions. The content of the macromonomer double bonds was determined independently using NMR spectroscopy and an iodometric titration method. The results of both methods are in excellent agreement for soluble samples. For samples containing gel particles, the titration method has significant advantages over the NMR spectroscopy. Only a part of the macromonomer double bonds reacts during the copolymerization, indicating that they are not very reactive. This means that there will be a considerable part of ungrafted polyurethane in the final hybrid product which might influence the application properties negatively. Batch experiments showed that the polyurethane macromonomers can homopolymerize in the absence of acrylate monomers. This is a surprising result because allylic groups are well known to show poor homopolymerizability, due to degradative chain transfer. The exact mechanism of this homopolymerization is still unknown.

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