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Kinetic Modeling from Early Product Development to Polymerization Process Optimization

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Summary: This contribution illustrates how kinetic modeling supports early product development stages under industrial constraints also for smaller scale products. Diisocyanate oligomerization is selected as an example. Data for model parameterization and validation are acquired in kinetic experiments with on-line IR monitoring. Based on these measured data and a proposed reaction scheme for the cyclo-oligomerization of diisocyanates with equal reactivity of both isocyanate groups, two kinetic models differing in level of detail are developed. All experimental trends are described correctly with these kinetic models. A functional group based model is used for parameterization and prediction of conversion profiles. This model version is also applied for assessing working hypotheses on the details of the catalytic cycle and for developing strategies for catalyst and process optimization. A second model takes into account full molecular weight distribution and thus enables prediction of individual oligomer concentrations. Fast assessment of process alternatives is possible with both models.

Keywords: diisocyanate; iminooxadizinedione; isocyanurate; kinetics (polym.); modeling; modification; molecular weight distribution; on-line IR spectroscopy; trimerization

Introduction

Numerous successful examples of modeling industrial polymerization processes have been reported.[1–3] Many examples apply to large scale production processes where reaction models are used for process control and operator training. This contribution illustrates how modeling efforts also support early product development stages and smaller scale products. Modeling in this case where material rather than engineering aspects dominate entails somewhat different challenges. The focus here is on the kinetic model rather than a full process model.

A sound mathematical model validated with experimental data can guide and complement experimental studies. Developing a kinetic model improves the understanding of underlying reaction mechanisms, e.g. catalytic processes. A better mechanistic understanding facilitates the design of experiments, supports recipe optimization and may reveal alternative synthesis strategies or alternative catalysts. As polymer molecular structure is controlled to a large extent by the reaction chemistry, a model can be used to find ways for customizing product properties by tuning molecular parameters like chain length distributions, chemical distributions, or stereoregularity. In early product development the main challenge is to provide a model sufficiently quickly so that model discrimination and simulation studies can still influence the experimental optimization process. The objective of such industrial modeling efforts is to shorten the time to market of a new product or new product grade by reducing the number of experiments that are necessary to synthesize a

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product with desired properties, and by increasing scale-up factors.

The approach described here is based on simultaneous experimental and modeling work. Experimental data are required for parameter estimation and to confirm or reject reaction schemes and corresponding model structures. The model can be used to evaluate competing working hypotheses and to select appropriate experimental conditions. In order to meet the requirement of a short model development time, the model has to be as simple as possible yet capture all relevant aspects of the reaction under industrially relevant conditions. The reaction and product parameters that have to be predicted determine the level of model complexity. As product and process development proceed the model is refined and becomes more detailed.

Diisocyanate oligomerization is selected as an example to illustrate model based support of product and process innovation under industrial constraints. Modified polyisocyanates containing free isocyanate groups are high quality building blocks for the production of polyurethanes, e.g. for coatings applications. Oligomers are the preferred raw materials because of their significantly lower vapor pressure compared to the corresponding monomer. The established industrial process for modifying isocyanates uses an oligomerization catalyst which is quenched once the desired degree of oligomerization has been reached. The residual monomer is separated from the product, e.g. by distillation, or extraction, and reused.[4] When applied to process development for modified polyisocyanates, a kinetic model can be used for determining the required residence time for a target degree of oligomerization and catalyst level at a given reagent quality. Optimization potential in terms of temperature control, catalyst dosage scheme, or reactor characteristics can be identified in simulation studies. In a product development sense, the model can provide information how to influence the composition of the polyisocyanate. Both aspects are discussed in more detail in the following.

Experimental Part

The diisocyanate used is hexamethylene diisocynanate (HDI) produced by Bayer MaterialScience AG, D-51368 Leverkusen. All kinetic experiments performed for model development were run with HDI from a single batch. Data from experiments with different HDI qualities were used for model validation. The polyfluoride oligomerization catalyst used is a proprietary catalyst developed by Bayer MaterialScience.

On-line IR spectroscopy is the main technique for monitoring product formation. A jacketed reactor with agitator and horizontal ATR crystal in the bottom plate of the reactor as depicted in Figure 1[5] is

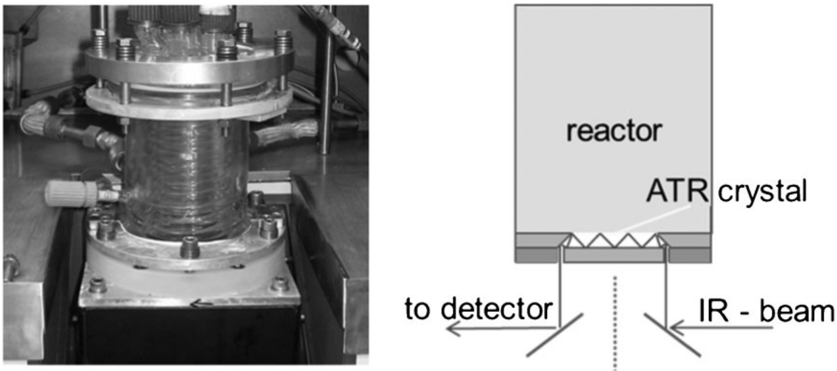

Figure 1.
Reactor used for kinetic experiments with on-line ATR-IR monitoring.

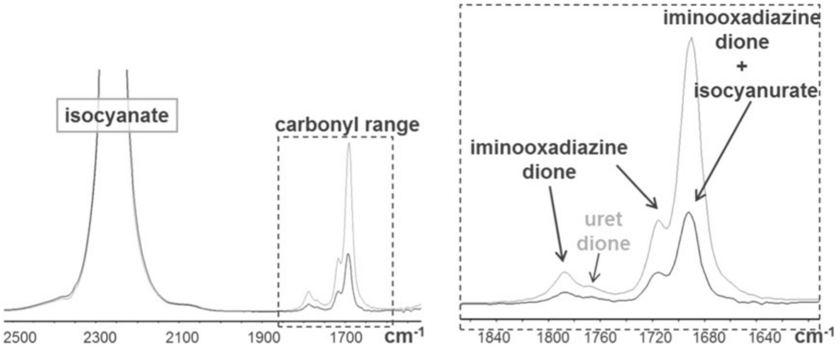

Figure 2.
ATR-IR spectra of products and potential byproducts measured in the reactor used for kinetic experiments.

used for the kinetic experiments. IR spectra are recorded every 4.1 seconds. HDI is preheated to the desired reaction temperature. The reaction is started by addition of the catalyst. The exothermic reaction causes an initial increase in temperature of 2–3 K. The first ca. 30% of the total conversion is made at this slightly elevated temperature before the temperature returns to the set point and is then maintained within a range of ± 0.3 K. Product concentrations are determined via quantitative analysis of the carbonyl signals for isocyanurate and iminooxadiazinedione as well as for side products like uretdione. Typical IR spectra are shown in Figure 2. The IR method is calibrated against product concentrations determined by chromatographic separation and quantification of oligomers. A linear relation between IR integration results and concentration is obtained. SEC (size exclusion chromatography) and titration are used for off-line characterization of final products. SEC analysis is performed according to DIN 55672-1.[6] Samples are dissolved in THF and diluted to $\leq$ 5 g/l. THF is also used as eluent. The column set with polystyrene-divinylbenzene stationary phase is maintained at 30 °C. Oligomer concentrations are measured by means of a refractive index detector. Quantification of individual oligomer species is achieved by calibrating with isolated oligomer fractions. Figure 3 illustrates a typical oligomer distribution from SEC. Total isocyanate content of oligomer samples is determined by titration according to DIN EN ISO 11909.[7]

Kinetic Model and Parameterization

Two different kinetic model versions were developed that focus on different aspects of the cyclo-oligomerization of diisocyanates. The cyclo-oligomerization of isocyanates produces different structures like uretdiones, isocyanurates, and iminooxadiazinediones (Figure 3) that significantly influence product properties. The ratio of these structures in the final product depends on the catalyst and on reaction conditions. For applications as crosslinking agents, NCO-trifunctional or higher functionality products are preferred, i.e. isocyanurate or iminooxadiazindione structures. A first model version aims at supporting synthetic efforts for maximizing the content of the lower viscosity (compared to isocyanurate) iminooxadiazinedione structure. This requires a kinetic model describing the formation of different structural units in the final product but not necessarily the full oligomer distribution. Therefore the first model version is limited to functional group balances for diisocyanates with isoreactive isocyanate groups. The reaction scheme is based on the mechanism reported for the phosphine-catalyzed cyclo-oligomerization of alkyl isocyanates.[8] The adapted reaction scheme as implemented in the kinetic model is depicted in Figure 4.

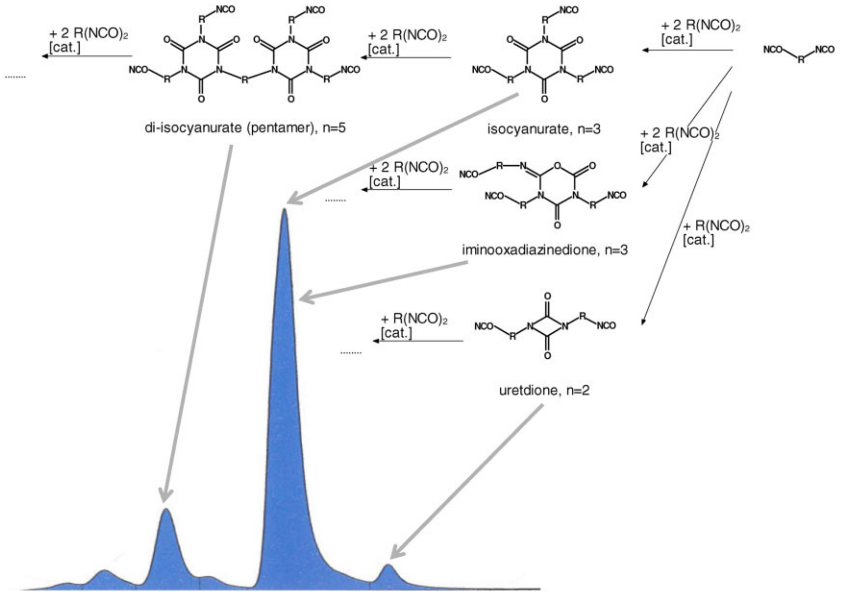

Figure 3.
Reaction scheme (simplified) for the catalyzed cyclo-oligomerization of a diisocyanate with isoreactive isocyanate groups, and corresponding oligomer distribution as analyzed by SEC.

In the first step, the catalyst adds to an isocyanate group on a monomer or oligomer (rate coefficient k1). This complex adds a second isocyanate group (rate coefficient k2). The addition of a third isocyanate group and the ring closure are represented as a single, concerted reaction. This is a model assumption for minimizing the number of required parameters. The addition of the third isocyanate group and the

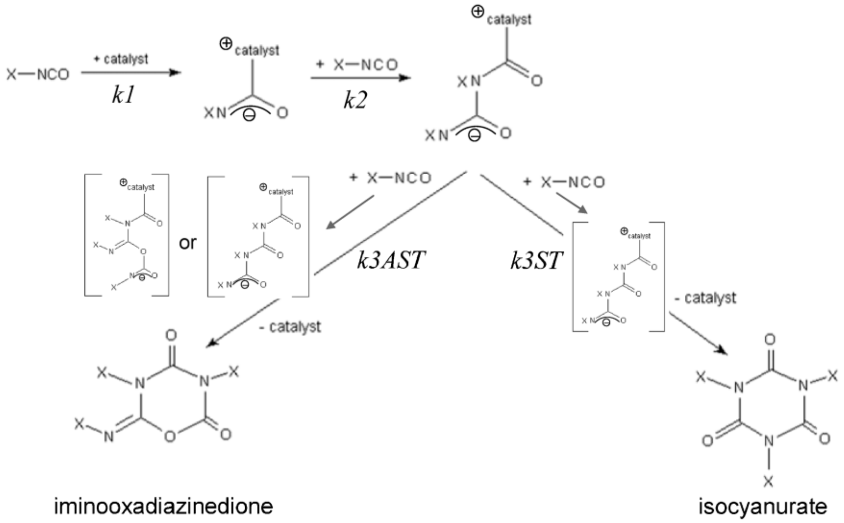

Figure 4.
Reaction scheme as implemented in the kinetic model and corresponding rate coefficients. Reactions involving monomers and oligomers are not distinguished in this representation. X denotes a fragment with at least one free isocyanate group (one in the case of monomer, multiple free isocyanate groups for oligomers).

ring closure may well be two separate steps, and/or the ring closure may also involve another isocyanate group or a catalyst-isocyanate complex. However, models taking into account multiple reaction steps could not improve the fit of the model to experimental data. Therefore the simplest version is implemented (rate coefficient k3). Another reaction that strongly influences the overall reaction rate is catalyst deactivation. The catalyst can deactivate in a purely thermal process, and by the reaction with catalyst poisons present in the starting material. The reaction with catalyst poisons is assumed to be faster than the reaction of catalyst with isocyanate groups. With this assumption the initial part of the conversion curve can be used for fitting the average catalyst poison concentration in the diisocyanate batch used in kinetic experiments. The slope of the conversion curve at long reaction time is affected by the thermal catalyst deactivation. Total product data (the sum of isocyanurate and iminooxadiazinedione concentrations) obtained at different catalyst concentrations are used for fitting the thermal deactivation rate coefficient, catalyst poison concentration and the rate coefficients k1 and k3. Since no measured data for reaction intermediates are available, the second reaction step is assumed to have no influence on the overall reaction rate and k2 is set to a value significantly larger than k1 and k3. The coefficients k1 and k3 are in the same order of magnitude with $k3 > k1$. All rate coefficients refer to a reaction first order in isocyanate functional group concentration and first order in catalyst (or catalyst complex, respectively) concentration. Figure 5 shows that simulation results for total product concentration profiles fit well to measured data.

In our kinetic model, the third reaction step differentiates isocyanurate (rate coefficient k3ST) and iminooxadiazinedione (rate coefficient k3AST) formation. The two rate coefficients in this reaction step as well as the reaction orders are the decisive parameters for the product distribution. Details of the elementary reaction steps involved in addition of a third isocyanate and ring closure may also differ for the two target structures. Figure 6 illustrates that a reasonable agreement between simulated and measured isocyanurate and iminooxadiazinedione concentrations is obtained with a simplified model assuming different rate coefficients and reaction orders for the formation of isocyanurate, and iminooxadiazinedione, respectively. Systematic deviations in the shape of the conversion curve indicate that the actual reaction mechanism is more complex than the one implemented in the kinetic model.

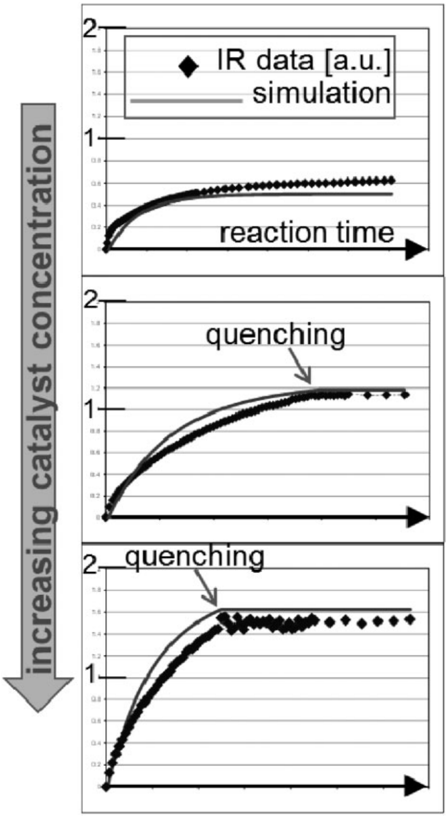

Figure 5.
Measured total product concentration from on-line IR monitoring (given as IR integration results in arbitrary units) in comparison to simulations with the functional group balance model described in the text.

A second version of the kinetic model targets the degree of oligomerization, and in particular the fraction of the ideal trimers ($n = 3$), as main product property. Since the

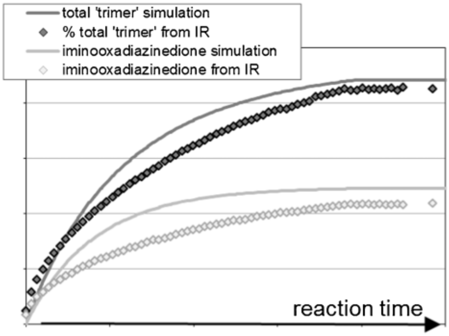

Figure 6.
Measured total product (isocyanurate + iminooxadiazinedione) concentration profile and iminooxadiazinedione concentration profile from IR monitoring in comparison to simulations with the functional group balance model described in the text.

cyclo-oligomerization forms multifunctional units and thus a crosslinking system that can form a gel, calculating the molecular weight distributions is a challenging task. A statistical approach as established by Schulz and Flory[9,10] can be used to compute the oligomer distribution as a function of monomer conversion. However, non-ideality cannot be easily taken into account in this way. Therefore, in an alternative approach, the kinetic model is extended to full molecular weight distributions. This model is implemented in the software package Predici that permits straightforward computation of full molecular weight distributions.[11] Even so the divergence of molecular weights at the gel point limits the applicability of the kinetic model. In order to analyze the influence of the kinetic scheme on molecular weight distributions, the kinetic model is simplified by assuming that beyond a critical degree of polymerization, oligomers are transformed into a gel with significantly reduced reactivity of isocyanate groups.

Results and Discussion

Results from simulations with the full molecular weight distribution model are compared to oligomer distributions calculated according to Schulz-Flory. When a reduced reactivity is assumed for all oligomers starting with the trimers ($n = 3$), simulated conversion dependent product distributions significantly deviate from Schulz-Flory predictions and from the measured data (Figure 7). Assuming gel formation and reduced reactivity at a degree of polymerization $n \geq 15$, the simulation results fit well to the measured data and even describe the deviations from Schulz-Flory predictions at high conversion. The measured data indicate that more ideal trimers and fewer higher oligomers than expected from statistics form at high monomer conversion. Different mechanisms are conceivable that restrict the formation of higher oligomers and hence justify the model assumption of a significantly reduced reactivity at higher

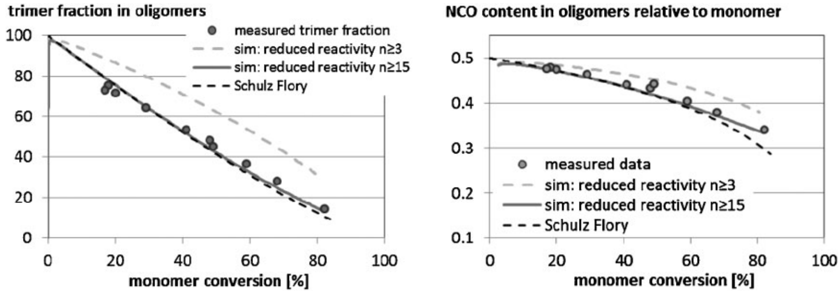

Figure 7.
Left: Measured (by SEC) and simulated trimer ($n = 3$) fractions in the product in comparison to Schulz-Flory predictions for the cyclo-oligomerization of a diisocyanate with isoreactive isocyanate groups. The different kinetic model versions are explained in the text. Right: Experimental (by titration) and simulated values for the resulting product isocyanate (NCO) content relative to monomer NCO content.

degrees of oligomerization. Such an effect can be attributed to a trapping of isocyanate groups in gel fractions (steric or diffusional limitations), or to the consumption of isocyanate groups in intramolecular reactions. Of course the choice of $n = 15$ as critical degree of polymerization in the model is somewhat arbitrary and a simplification. An increasing retardation with increasing degree of polymerization is probably more realistic but not straightforward to implement and parameterize.

The simulated oligomer distributions as a function of conversion are shown in Figure 8. Only at the highest conversion shown (60%) small differences between the statistical (Schulz-Flory) distribution and the one from the kinetic model are detectable. However, the polydispersity changes significantly because of changes in high oligomer ($n > 11$) contributions. Experimental data from SEC become less accurate with increasing degree of oligomerization because the analytical method applied here is optimized for a reliable quantification of the first few oligomers and has an exclusion limit at rather low degree of oligomerization. Therefore, neither the experimental polydispersity from SEC nor the data for individual oligomer concentrations in the range of $n > 11$ where larger differences between statistics and kinetic model can be seen are reliable. However, taking all available analytical data into account, the experimental trends confirm the simulation results that show a reduced polydispersity.

The kinetic models can be used to assess different production process options. To illustrate this application, simulations for two extremes are presented in Figure 9. An ideally mixed continuous stirred-tank reactor (CSTR) is compared to a plug flow reactor without backmixing. As expected for a reactor with broad residence time distribution, polydispersity in the CSTR is much higher and product isocyanate content much lower than for products from a reactor without backmixing. In addition to predicting product properties at a given conversion, the kinetic model can also be used for determining, e.g. the required reactor volume for achieving a target conversion with a given mixing characteristic.

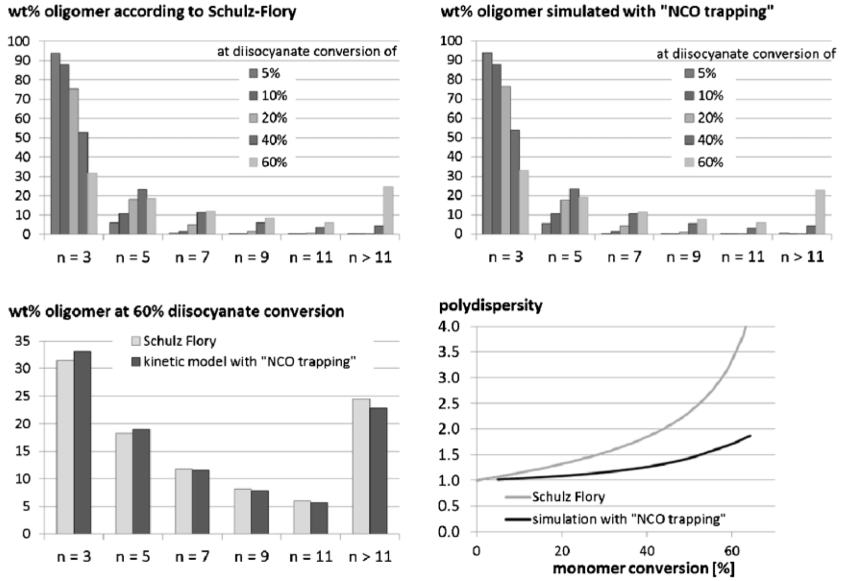

Figure 8.

Oligomer distributions as a function of diisocyanate conversion for a reaction scheme according to Figure 3. Schulz Flory predictions in comparison to simulation results from the kinetic model with reduced isocyanate reactivity for higher oligomers ("NCO trapping").

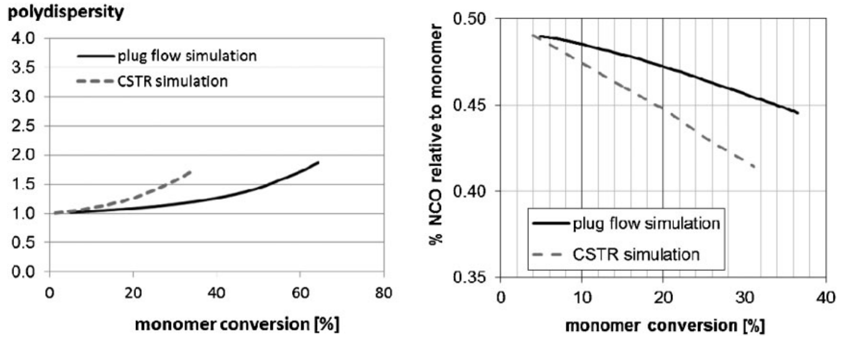

Figure 9.

Application of the full molecular weight distribution model for comparing product properties from two ideal reactor types, a continuous stirred-tank reactor (CSTR) and a continuous reactor with plug-flow profile.

Conclusion

Two kinetic models differing in level of detail have been developed. All experimental trends are described correctly with these kinetic models. The simplified, functional group based model is used for assessing working hypotheses on the details of the catalytic cycle and strategies for catalyst and process optimization. Work on a more detailed model for providing an accurate description of parameters influencing the product distribution is in progress.

The full oligomer distribution model predicts well overall conversion and oligomer distributions. It can be used for a fast assessment of process alternatives, or for estimating required residence time as a function of catalyst concentration and starting material quality. For the example of hexamethylenediisocyanate oligomerization presented here, the model has supported the development of an efficient production process.

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