Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Rätzsch, M. , Bucka, H. , Hesse, A. and Arnold, M.(1996) 'Basis of Solid-Phase Grafting of Polypropylene', Journal of Macromolecular Science, Part A, 33: 7, 913 — 926
To link to this Article: DOI: 10.1080/10601329608014641
URL: http://dx.doi.org/10.1080/10601329608014641

J.M.S.—PURE APPL. CHEM., A33(7), pp. 913–926 (1996)

BASIS OF SOLID-PHASE GRAFTING OF POLYPROPYLENE

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INTRODUCTION

The chemical modification of polymers opens new dimensions for the development and design of materials based on plastics. The chemical modification of polymers by reactions is performed by reactions in a melt, in a solution, or in a solid phase. The modification of polymers in solid phases (powder or granular material directly from the polymerization) has great advantages compared with reactions in solution or melt. The advantages are lower costs and, most important, greater creative variability. A special advantage of solid-phase modification of polypropylene (PP) is the fact that the degradation reaction is reduced.

Figure 1 shows the relative rate of the β-scission of PP [14, 15]. It can clearly be seen that under conditions of solid-phase modification ($T \sim 100°C$), β-scission can be neglected. However, under conditions of melt modification ($T \sim 200°C$), β-scission has a significant importance.

The topics presented in this paper are diffusion and sorption of radical initiators and monomers in polypropylene, and kinetics of the propagation and termination reactions in the amorphous phase. The investigation of these processes is necessary for the determination of the possibilities and limits of this technology, as well as for the development and optimization of process technology.

TRANSPORT OF THE COMPONENTS TO THE REACTION SITE

Morphology of Native PP Powder

The increase of the chemical reactivity of the active centers of catalysts, along with the formation of a solid-phase structure which doesn't hinder material trans-

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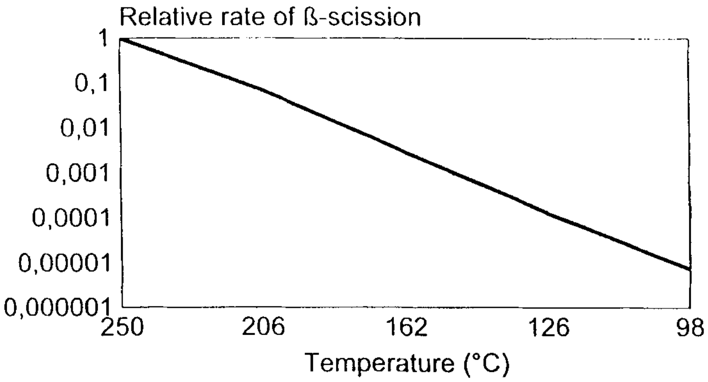

FIG. 1. Dependence of the relative rate of β-scission of PP (in relation to 250°C) on temperature.

port of the monomers to the reaction site, was an important precondition for the increase of the activity of the catalysts.

According to a conception (developed for the first time by Yermakov et al. [1]), carrier catalysts consist of a porous support with a multitude of active centers which quickly break into small pieces at the beginning of polymerization. During this process the association of the catalyst particles remains. During the polymerization process at the active centers, microparticles arise which form polymer grains in association with the microparticles. This concept is the basis for the "multigrain" model [2, 3] (Fig. 2).

Electron microscopic investigations and measurements were made of the sorption rate of Daplen PP powder from PCD. Figures 3 and 4 clearly show the "multi-

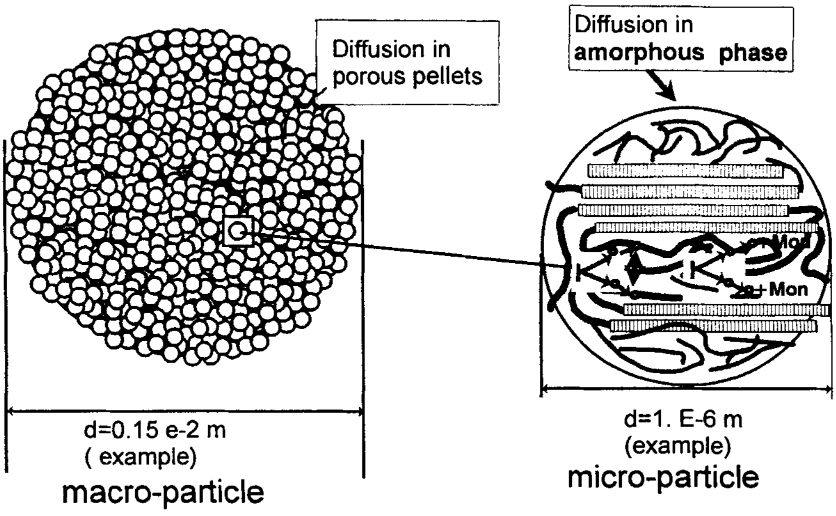

FIG. 2. Multigrain model.

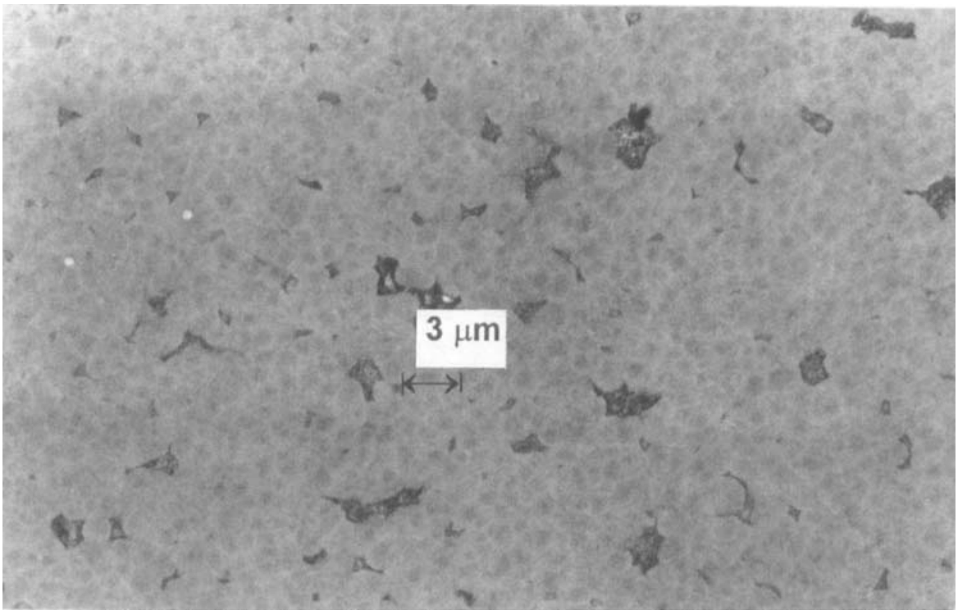

FIG. 3. PP-granule as agglomerate of microparticles, 17,200×.

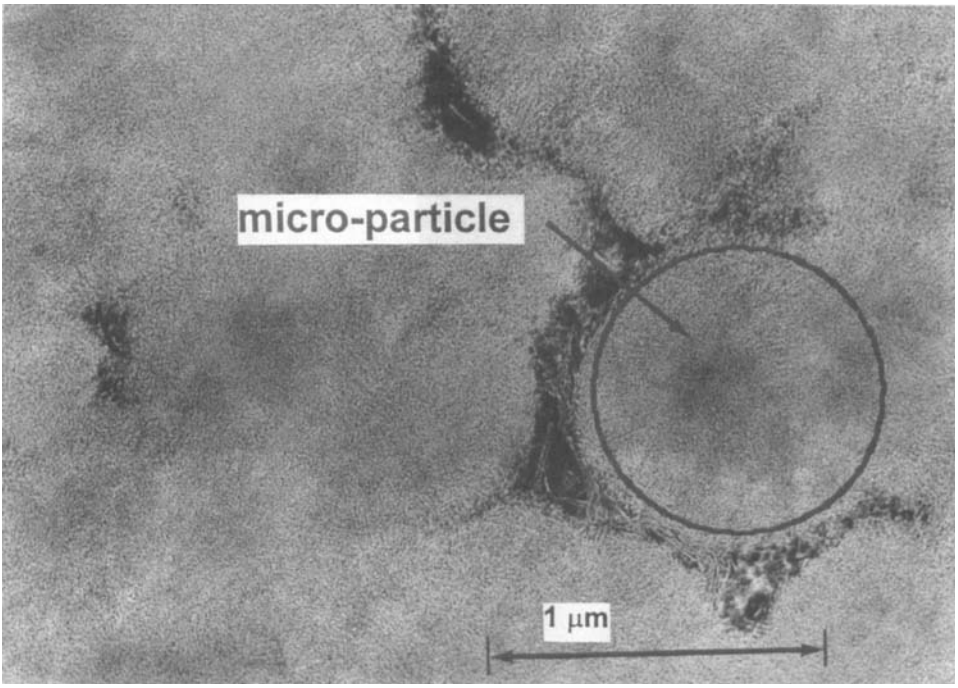

FIG. 4. Microparticle in the PP-granule, 57,500×.

grain" structure of PP synthesis products. The size of the microparticles and the dimension of the cavities can be estimated from Fig. 4. The diameter of the microparticles is between approximately 0.5 and 1 μm. The cavities have a width of approximately 0.08 μm. These values can be taken as examples, but they are not valid for all products.

During the transport of the components to the reaction site, the following processes occur:

Diffusion in the pores of the PP grain
Mass transfer from the gas phase to the surface of the microparticle
Adsorption in the amorphous phase
Diffusion in the amorphous phase of the microparticle

Basic examinations by other authors [12] show that sorption and diffusion in the crystalline range can be neglected. Reactive modification by solid-phase grafting can only take place in the amorphous regions.

Diffusion in the PP Grain

Measurements of the sorption rate using different modificators to determine the diffusion rate in the PP grain were performed by Kietz et al. [5]. The apparatus used is described in Ref. 7.

Figure 5 depicts the components styrene and butadiene as an example of a typical sorption process and the determination of effective diffusion constants. A supposition for this analysis is that the PP grain is homogeneous. Under this precondition, an apparent diffusion constant for the homogeneous PP grain can be determined which includes both the material transport in the pores and the material transport in the amorphous phase.

This one parametric model reproduces exact results (with an error <2%). An exact physical interpretation of the results and the separation of the single transport resistances is not possible.

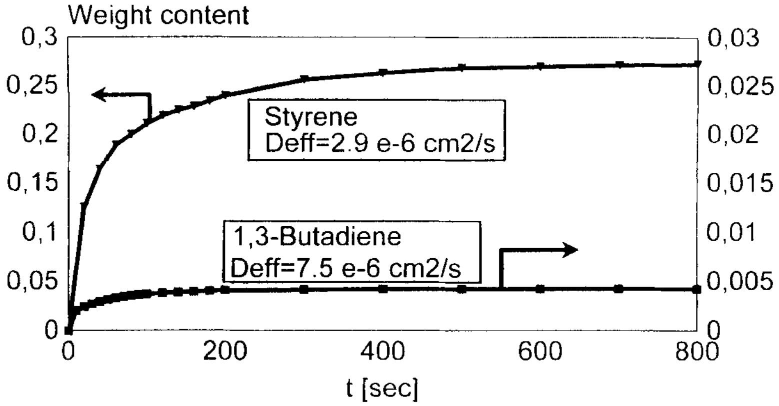

FIG. 5. Dependence of the weight content (in the solid phase) of styrene and butadiene on time.

TABLE 1. Diffusion Coefficients of Solvents and Monomers in PP

Solvent/monomer	Polymer	Morphology		Temperature (°C)	Diffusion coefficient, cm^2/s	Reference
		Compact	Powder (porous)			
Toluene	PP	×		50	1e-8	4
Methylcyclohexane	PP	×		50	5e-9	4
Styrene	PP		×	70	0.93e-6	5
1,3-Butadiene	PP		×	70	0.9e-5	5
Propene	PP	×		70	1e-8 to 1e-6	3
Propene	PP	×			1e-8	11
Propene	PP		×	70	1e-4 to 1e-3	3

Our effective diffusion constants are compared in Table 1 with results from the literature. Our diffusion constants are higher than constants for diffusion in amorphous phases. They are comparable with reported effective diffusion constants [3, 11] for diffusion in macroparticles during polymerization in the PP grain.

Figure 6 shows the dependence of effective diffusion constants on the molecular weight M of the modification components. It is concluded that for diffusion in a porous grain, the equation $D_{\text{eff}} \sim 1/M$ is valid.

Sorption of the Modifiers

To describe the sorption of solvents in polymers, various thermodynamic examinations have been undertaken and a multitude of models have been suggested. The possible extent of the experimental examinations is restricted, and therefore a

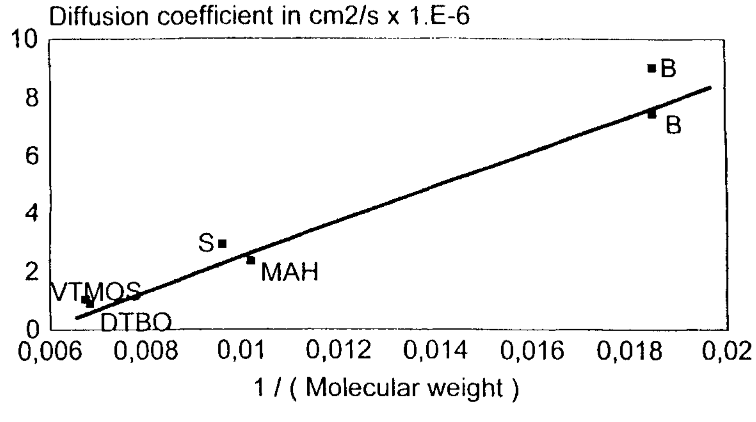

FIG. 6. Relation between diffusion coefficient and molecular weight.

special model was chosen for the description of the sorption. This model allows calculations of the correlations on the basis of limited experimental data. The model has not only to describe interpolatively, but also extrapolatively, in higher temperature and pressure ranges.

Regener [16] used the chain-of-rotators-state-equation (COR) for polymers and installed an additional group contribution concept. Fink et al. [13] successfully proved the feasibility of relating different monomer/copolymer phase equilibriums.

The binary interaction parameters can be determined by using adjustments of the COR model with the Henry constants which are the result of IGC measurements. The model doesn't include ternary interaction parameters.

RESULTS OF EXPERIMENTAL EXAMINATIONS

The determination of the Henry constants was made by inverse gas-liquid chromatography (IGC) by Wohlfahrt [7].

The Henry constant H as related to the mass fraction can be directly calculated from the reduced corrected retention volume:

$$H = R \cdot 273.15/(M \cdot VgO)$$

M is the molar mass of the respective solvent, VgO is its corresponding retention volume, and R is the general gas constant.

Table 2 shows the results of the experimental determination of the Henry constants. In the temperature range examined, a linear dependence of ln H versus $1/T$ was found (Fig. 7).

In Fig. 8 the results of sorption measurements for ethylbenzene/propylene homopolymer and ethylbenzene/random ethylene–propylene copolymer are shown. Obviously, the PP type influences the solubility very strongly. The solubility of ethylbenzene in copolymers is much higher. The ascertained data are valid for sorption from the gas phase. The data are thermodynamically identical with those from the liquid phase at the same temperature.

In Fig. 9 the results from the calculations of the equilibrium solubility of styrene in PP and butadiene in PP with the COR model and with the Henry equation are compared. The description of sorption by the Henry equation is only satisfactory at low solubilities.

Figure 10 shows the weight content of sorbed styrene and butadiene related to PP in dependence on temperature at constant pressure of monomers. It is evident that the solubility of monomers decreases with increasing temperature.

Calculation results of the equilibrium solubility of styrene and butadiene in PP in dependence on temperature are depicted in Fig. 11. By varying the process conditions, especially the system pressure/temperature, the concentration of modifiers in the amorphous phases of PP can be regulated.

KINETICS OF PROPAGATION AND TERMINATION REACTIONS IN THE AMORPHOUS PHASE

Basics

Up to now, investigations concerning the kinetics of propagation and termination reactions of the graft process in the solid phase of a polymer have not been made. From theoretical considerations it can be shown that the terminating reac-

TABLE 2. Henry Coefficients of Different Solvents/Monomers in PP

Solvent/monomer	Temperature in K	*H* in MPa
Ethylbenzene	333.15	0.0618
	353.15	0.1357
	373.15	0.2591
	393.15	0.4603
	413.15	0.7712
	433.15	1.1080
Styrene	333.15	0.0420
	353.15	0.0900
	373.15	0.1768
	393.15	0.3260
	413.15	0.5412
	433.15	0.8587
1,3-Butadiene	333.15	5.750
	353.15	8.833
	373.15	13.05
	393.15	17.20
	413.15	23.50
	433.15	29.10

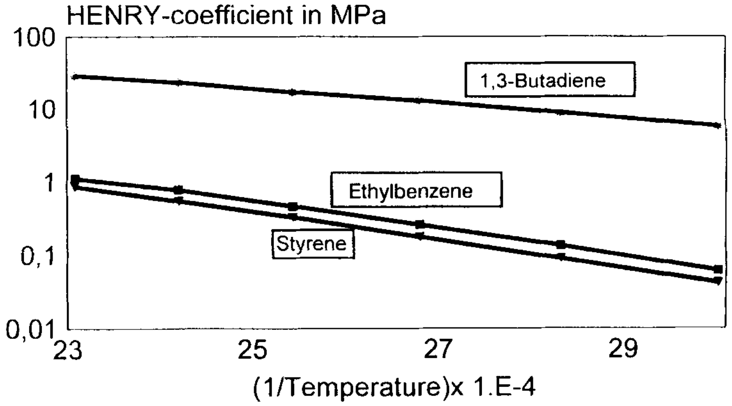

FIG. 7. Relation between Henry coefficient and temperature.

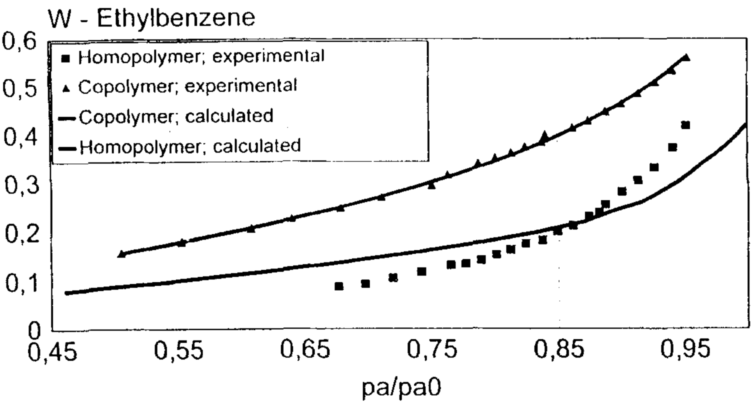

FIG. 8. Solubility of ethylbenzene in PP. Comparison of experimental results with calculated data (COR model).

tions are hindered, analogously to the Trommsdorff effect at high conversions in the mass polymerization process.

We investigated the polymerization behavior of styrene sorbed in PP because the reaction rate constants of styrene polymerization are relatively well known.

Description of the Experiments

The PP powder was evacuated and purged with argon to remove the oxygen. Then it was stored under argon atmosphere.

The sorption of the styrene-peroxide mixture was done in the liquid phase. For that purpose, distilled styrene which contained the peroxide was added to the PP powder. Sorption was carried out in a tempered glass flask for 1 hour. Then the

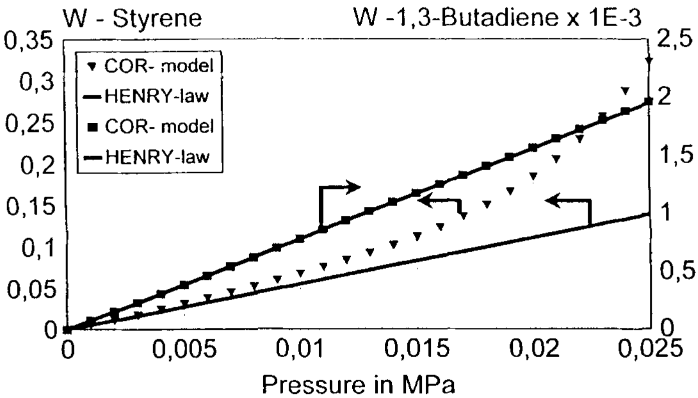

FIG. 9. Comparison of calculated data according to the COR model with calculated data according to Henry's law.

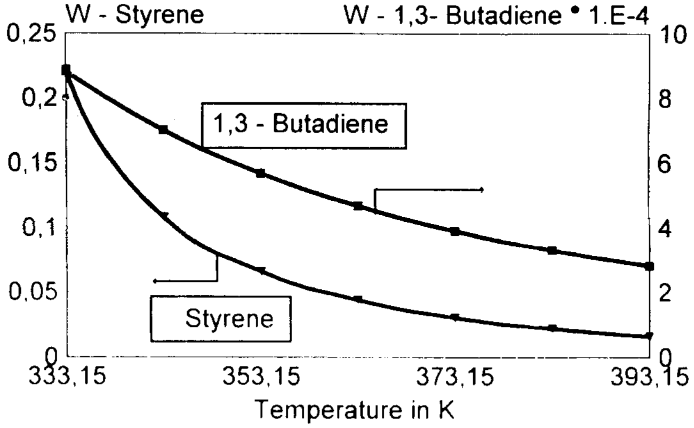

FIG. 10. Dependence of weight content (ww) in the solid phase on temperature (pressure → constant = 50 kPa).

glass flask was heated up to the reaction temperature in an oil bath. The polymerization of styrene in the solid phase of PP was followed by sampling with a specially prepared sampler under inert conditions. After sampling, the polymerization was stopped by introducing the powder into methanol which included 1% Ionol. Then the sample was separated by filtering and dried in vacuum at 60°C for 24 hours. The conversion degree of polymerization was gravimetrically determined.

Results

The progress of styrene polymerization in PP in dependence on time is shown in Fig. 12. The experimental data are the basis for process interpretation.

A kinetic model which considers the nonisothermic character of our experiments was used for simulation of solid-phase grafting. Mass transfer processes are

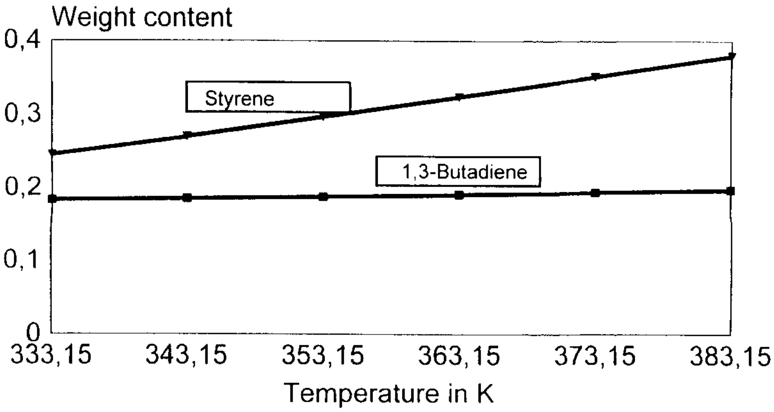

FIG. 11. Dependence of weight content (ww) in the solid phase on temperature (pressure = vapor pressure).

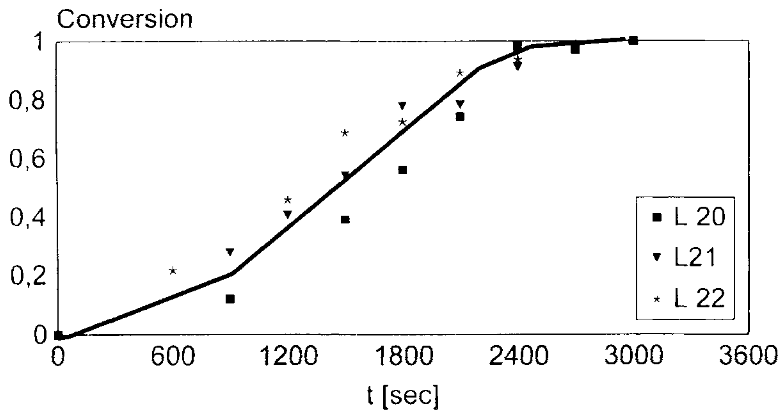

FIG. 12. Experimental results of conversion-time dependence.

not included because the sorption of styrene and peroxide in PP is carried out in a separate step before graft polymerization.

The reaction mechanism taken as the basis of our simulation model is described in Table 3. The temperature dependence of rate constants is given by the Arrhenius equation:

$$k_{xx} = A_{xx} \cdot e^{-E_{xx}/R \cdot T}$$

Published values for reaction constants of the elementary reactions of styrene polymerization are listed in Table 4. Data were used as initial values for our calculations.

TABLE 3. Mechanism of Radical Grafting Reaction

Decomposition of peroxide	$I_1 \xrightarrow{k_d} 2R^{\cdot}$
Hydrogen abstraction	$R^{\cdot} + PP{-}H \xrightarrow{k_{tr}} R{-}H + PP{-}(0,\bullet)$
Start	$R^{\cdot} + S \xrightarrow{k_i} S(1,\bullet)$
Propagation	$PP{-}S(j,\bullet) + S \xrightarrow{k_p} PP{-}S(j+1,\bullet)$ $S(j,\bullet) + S \xrightarrow{k_p} S(j+1,\bullet)$
Termination by recombination	$PP{-}S(j,\bullet) + PP{-}S(j1,\bullet) \xrightarrow{k_t} PP{-}S(j+j1,\circ)S{-}P$ $PP{-}S(j,\bullet) + S(j1,\bullet) \xrightarrow{k_t} PP{-}S(j+j1,\circ)S$ $S(j,\bullet) + S(j1,\bullet) \xrightarrow{k_t} S(j+j1,\circ)S$

TABLE 4. Rate Constants of Styrene Polymerization

Reaction	Frequency factor	Activation energy[a]	Source
Decomposition of peroxide, k_d	7.09e+14	123.6	9
Propagation, k_p	7.2e+6	29.3	10
Termination, k_t	1.3e+9	10.1	10
Termination (hinderd), k_{th}	0.65e+6	10.1	8
C_{RD}	800		

[a] $R = 8.315$ kJ/(grd·kmol) ($k_{xx} = A_{xx} \cdot e^{-E_{xx}/RT}$).

Figure 13 shows the calculated curve of the time-conversion dependence of styrene polymerization with unhindered termination reaction. Considerable deviation between the experimental points and model curve can be seen. The rate of styrene polymerization in the solid phase of PP is much higher than polymerization with an unhindered termination in solution. A description of our experimental data by a simple kinetic polymerization model is not possible.

The curve drawn in Figure 14 as a solid line is calculated on the basis of a kinetic model with a hindered termination reaction in which a rate constant from the literature is used [8]. Comparison of the graph shows that the calculated conversion is higher than the experimental data, especially at the beginning of reaction. In Fig. 14 it is also shown that by using a stepwise increase of the rate constant of the hindered termination, the slopes of the model curves can be reduced, but the shapes of the calculated curves are still not adequate to define the course of the experimental data.

According to Schulz [8], the dependence of the termination rate on the conversion can be described by

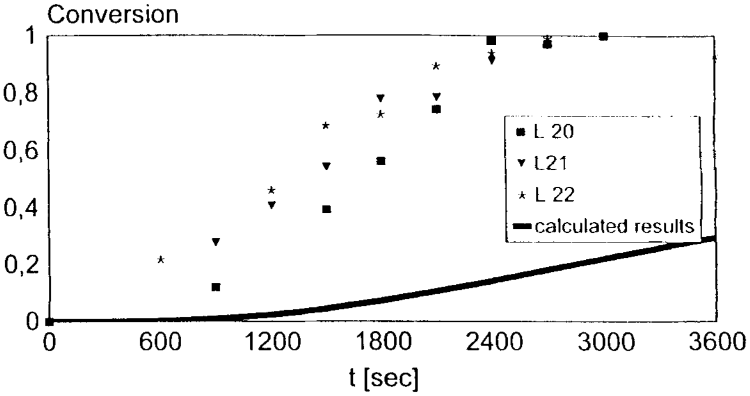

FIG. 13. Comparison of observed with calculated results of conversion (termination = solution polymerization).

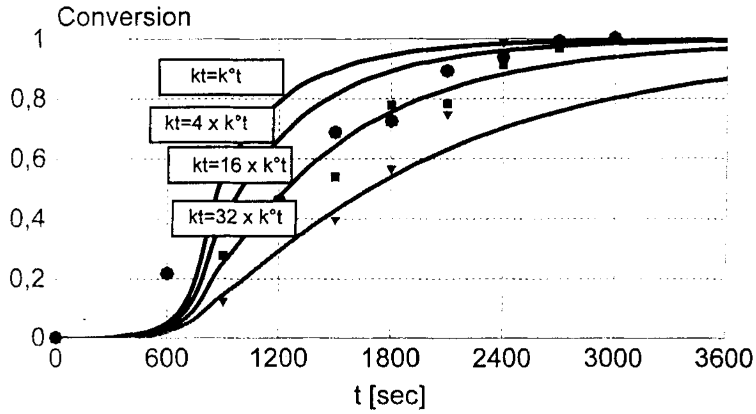

FIG. 14. Comparison of observed with calculated results of conversion (influence of termination constant).

$$U = \frac{C_m^o - C_m}{C_m^o} \rightarrow C_m = C_m^o \cdot (1 - U) \rightarrow (1 - U) = \frac{C_m}{C_m^o}$$

$$\begin{aligned} k_t &= C_{RD} \cdot k_p \cdot (1 - U) \\ &= C_{RD} \cdot k_p \cdot \frac{C_m}{C_m^o} \\ &= \frac{C_{RD}}{C_m^o} \cdot k_p \cdot C_m \end{aligned}$$

The physicochemical background of this relationship is based on the idea that the termination reaction proceeds by radicals which become nearer and meet by chain growth. This model can be transformed to reactions in the solid phase. C_m is the styrene concentration which arises by sorption in the amorphous phase of PP.

Figure 15 shows the calculated time–conversion dependency. The calculated conversion can be adjusted to the experimental data by changing the model parameters when considering the conversion dependence (according to Schulz). The calculated curve is a good description of the process.

CONCLUSIONS

Diffusion and equilibrium sorption play an important role in solid-phase grafting. It is possible to determine equilibrium sorption and diffusion of several components with the methods we have discussed. The combination of kinetic and thermodynamic measurements along with a modern thermodynamic model has proved effective. Using the supposition and approximation of modeling has proved to be acceptable. Therefore, it is possible to obtain a general view of the behavior of modifiers in a PP particle. One parametric model was sufficient to describe the diffusion rate. The best manner to describe the experimental data is through separation of the transport resistances: *diffusion in pores* ↔ *diffusion in the amorphous range*. The results of these examinations show that polymerization in the amorphous

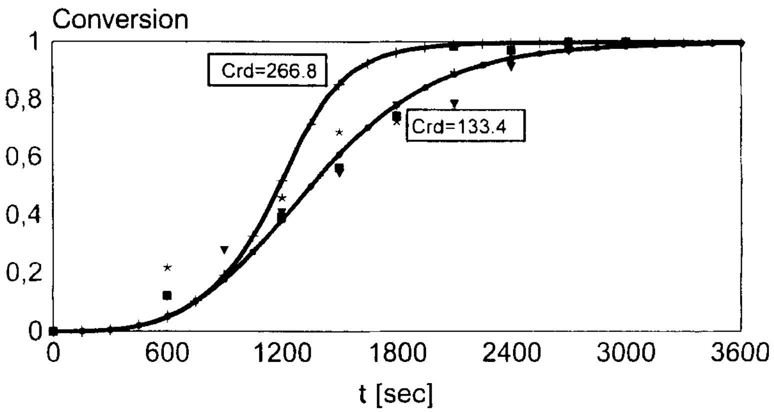

FIG. 15. Comparison of observed with calculated results of conversion (influence of the C_{RD} parameter on conversion).

PP phase is strongly accelerated compared with polymerization in solution. It was proved through model calculations that restriction of the termination reaction was the reason for polymerization acceleration. It was possible to reproduce the results of the experiments by variation of the physical range of the model parameters.

To improve the parameter adaption, it is necessary to improve the precision and reproduction of experimental results along with the simultaneous adaption of several parameters.

ACKNOWLEDGMENT

The research was supported by the "Forschungsförderungsfonds für die gewerbliche Wirtschaft" of the Republic of Austria.

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