Influence of Pigment Properties on UV-Curing Efficiency

Lavinia Macarie,[1] **Gheorghe Ilia**[1,2]

[1]*Institute of Chemistry Timisoara of Romanian Academy, 300223 Timisoara, Romania*
[2]*Faculty of Chemistry, Biology and Geography, West University, 300115 Timisoara, Romania*

Received 26 May 2006; accepted 7 September 2006
DOI 10.1002/app.25563
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The curable formulations containing monomer-diacrylate, photoinitiator-*p*-methoxybenzoyldiphenylphosphine oxide/benzyldimethylketal, additive reactive-triethylamine, and inorganic thermoresistant pigments-white, red, green, and blue were cured by UV exposure films. A series of experiments was carried out to investigate the relationship between the particle size distribution of the inorganic pigment and the colorimetric and mechanical properties of the UV acrylic curable coatings. Pendulum hardness and appearance of the films depend on the content and particle size distribution of the pigment. Optimal particle size distribution and pigment content were established to obtain the best films concerning their pendulum hardness and chromatic parameters. J Appl Polym Sci 104: 247–252, 2007

Key words: UV curable formulation; pigmented coatings; photoinitiators; film properties

INTRODUCTION

For more than 20 years, photoinitiators for UV-curable coatings have been successfully used in the coatings industry for varied applications such as coatings for furniture and flooring, inks, plastic decoration, optical fiber coating, adhesives, and electronics.

This expansion into applications is due to some basic advantages such as high speed process, low energy consumption, reduction of pollution (absence of the solvent), good cost/performance relation, and high chemical and mechanical strength.

Organophosphorus compounds, such as acylphosphonates and acylphosphine oxides, were developed as a new class of photoinitiators. They are very effective in radical polymerization of unsaturated monomers (acrylates, styrene, epoxy resins, and unsaturated polyesters) to obtain both transparent and colored coatings.[1,2] Acylphosphonates and acylphosphine oxides can be improved through cure.[3] These photoinitiators can be used either alone or in combination with other photoinitiators, i.e., α-hydroxy ketones (HK) or benzyldimethyl ketal,[4] which give a good surface cure.[5]

In the area of coloring materials, organic dyes and inorganic pigments are used.

The appearance of the coated object (e.g., color, gloss) is a complex function of the light incident on the object, the optical scattering characteristic of the material, and human perception. Pigments are very fine powders being nearly insoluble in binders and solvents, but provide color and the ability to hide the underlying surface.

The mechanical properties of the coatings [i.e., pendulum hardness (PH)] may be affected by the presence of the inorganic pigment and by its physical properties. Pigment will affect the photoinitiator absorption characteristics by competing with the latter for the incident radiation. This can be understood in terms of scattering effects, film thickness, substrate type, and pigment color characteristics. However, the inorganic pigments imply certain advantages versus organic dyes, such as intensity of color, hiding power, thermal and chemical resistance, and absence of migration effect.[6]

Moreover, using formulation based on acrylic monomers are obtained UV-cured coatings with some performance characteristics such as reactivity, gloss, adhesion, chemical resistance, scratch resistance, abrasion resistance, and nonyellowing.[7]

In this article is reported the influence of the pigment on the appearance and mechanical properties of the UV-cured acrylic coatings, using 4-methoxybenzoyl diphenylphosphine oxide, previously reported as a new effective photoinitiator.[8] The particle size, content, and natural color of the pigment were the studied parameters.

EXPERIMENTAL

The base curable formulation contains

- Monomer: Photomer 3016 40T (Henkel)—Bisphenol-A epoxydiacrylate—commercial product for coatings.

Correspondence to: G. Ilia (ilia@acad-icht.tm.edu.ro).

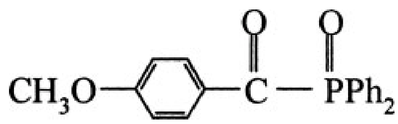

Figure 1 Photoinitiator *p*-methoxybenzoyldiphenylphosphine oxide (MBDPPO).

- Photoinitiator: *p*-Methoxybenzoyldiphenylphosphine oxide (MBDPPO) 2.5 wt % versus monomer (Fig. 1) and 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba-Geigy) 0.5 wt % versus monomer.
- Additives: Triethylamine as synergist additive at 3 wt % versus monomer.[9]
- The following pigments samples were chosen; white: TiO_2, red: cadmium sulfoselenide, green: TiO_2-NiO-ZnO, blue: Al_2O_3-Cr_2O_3. The pigment particle size (d) distribution ranged in: $d < 5$ μm, 5 μm $< d <$ 50 μm, and 50 μm $< d <$ 90 μm domains.

To provide adequate hiding power of the pigmented formulation, the pigment content has been chosen in the range of 5–15%. Up to 15% pigment content may affect the efficiency of photoinitiator. The hardness of the pigment powder may influence the PH of the cured coating. Hence, it was determined that the hardness of the pigment powder increases, qualitatively, in the following order: white, red, green, and blue.

The formulation was laid on glass panel with a film applicator to obtain films of thickness 120 μm.

UV-curing was carried out with a medium pressure mercury vapor lamp (80 W cm^{-2}, belt speed 3 m min^{-1}).

The polymerization efficiency/conversion and polymerization rates of UV-curing systems containing pigments were performed by differential scanning photocalorimetry (photo-DSC) in comparison with the original systems without pigments. Photo-DSC was performed using a DuPont 930 irradiation unit with a double head differential calorimeter 912 calibrated with indium metal standard. A standard high pressure Hg lamp with 3 mW cm^{-2} light intensity was used for sample UV exposure. The experiments were carried out under inert atmosphere N_2.

PH was determined with Koenig pendulum (DIN 53157).

Color measurements of the cured films were carried out by trichromatic colorimetric methods CIE and HunterLAB. The color is obtained by additive combination of three basic trichromatic components X, Y, Z, experimentally determined using colorimeter, in accordance with CIE system. The sample (pigmented film) is directly illuminated by a single wave length of light.

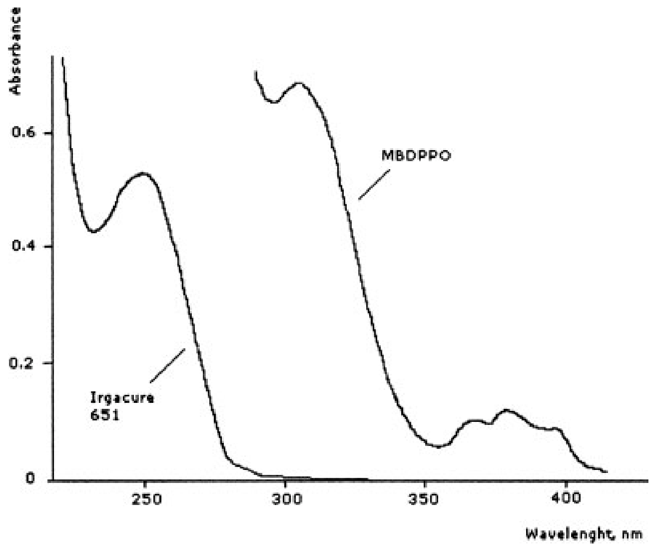

Figure 2 Absorption spectra of MBDPPO and Irgacure 651 ($c = 1 \times 10^{-4}M$ in acetonitrile).

The selected parameters to characterize chromatic appearance are[10,11]

- color brightness, L [eq. (1)]:

$$L = 10Y^{1/2} \quad (1)$$

- a, red hue for positive values or green degree for negative values [eq. (2)];

$$a = [17.5(X/0.98041) - Y]/Y^{1/2} \quad (2)$$

- b, yellow hue for positive values or blue degree for negative values [eq. (3)].

$$b = [7.0Y - (Z/1.18103)]/Y^{1/2} \quad (3)$$

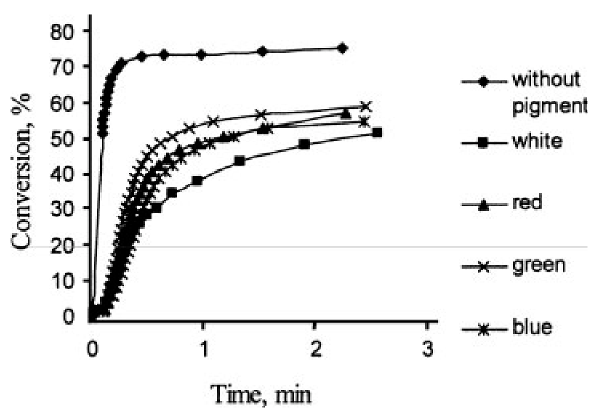

Figure 3 Conversion versus exposure time for different pigment (pigment content 5%, particle size $d < 5$ μm) in comparison with the system without pigment.

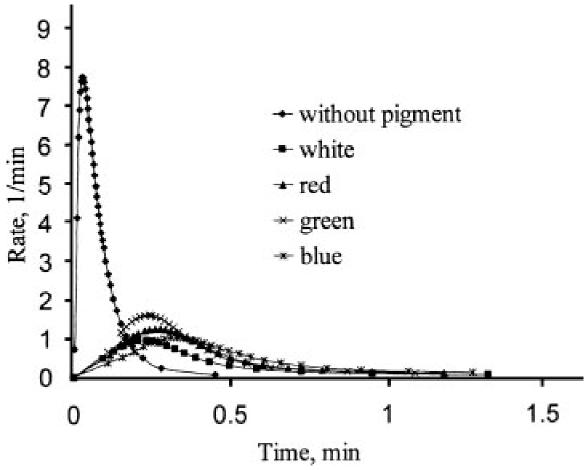

Figure 4 Rate of polymerization versus exposure time for different pigments (pigment content 5%, particle size $d < 5$ μm) in comparison with the system without pigment.

RESULTS AND DISCUSSION

Absorption characteristics of photoinitiators

In Figure 2 are shown the absorption spectra of the photoinitiator MBDPPO and Irgacure 651. Acylphosphine oxide (MBDPPO) appears to be efficient, mainly because of its superior absorbance in the near-UV range. This class of photoinitiators proved to be particularly well suited for the UV-curing of pigmented systems, in comparison with Irgacure 651. A mixture of photoinitiators MBDPPO and Irgacure 651 was used to obtain both through cure and surface cure.

Photo-DSC measurements

Conversion and rate of polymerization versus exposure time are presented in Figures 3 and 4, respectively.

The presence of the pigment in photopolymerizable formulation led to an expected effect: the decrease of monomer conversion and polymerization rate in comparison with the formulation without pigment. However, good values for conversion are obtained after less than 3 min of exposure.

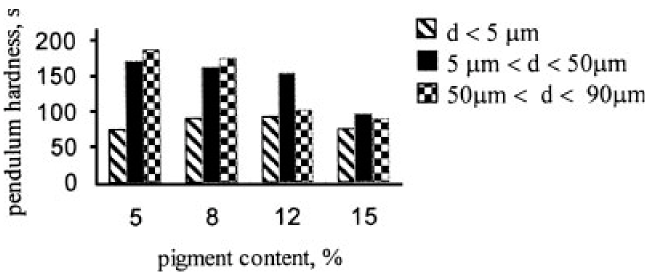

Figure 5 Pendulum hardness functions of white pigment particle size at different pigment content.

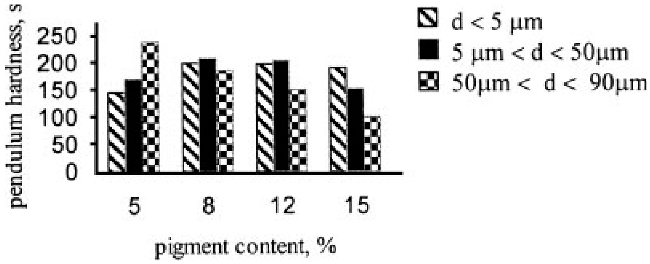

Figure 6 Pendulum hardness functions of red pigment particle size at different pigment content.

Mechanical properties of the films

If MBDPPO is used as photoinitiator, the PH of the clear coating is 235 s.[8] Figures 5–8 summarize the UV-curing results considering different particle size distribution of pigment and various pigment content.

Film PH depends both on pigment content and particle size. A comparison between PH of pigmented films for all color leads to the conclusion that film PH is in accordance with pigment powder hardness, the hardest films are those that are blue in color.

Generally, for each color and pigment content, granulation $d < 5$ microns induced lower values of PH of pigmented films versus transparent films (without pigment). In case of blue pigment the values of PH were higher due to higher hardness of pigment powder. It can be explained in terms of the high homogeneity of the low size particle system and, probably, the presence of the particles of the pigment have the tendency to interrupt the increasing of polymer chain and, hence, leading to the decreasing of molar weight of the polymer.

Granulation 5 μm $< d <$ 50 μm induced moderate values of PH and their variation is likewise in the case when granulation $d < 5$ μm. Granulation 50 μm $< d <$ 90 μm led to higher values of PH at 5 and 8% pigment content and low values at 12 and 15%. In the latter case, the scattering effects are more important due to great dimension of the particle size. Therefore, the photoinitiator efficiency is diminished and conversion decreased. The dependence of PH-pigment content at granulations $d < 5$ μm (Fig. 9) and 5 μm $< d <$ 50 μm (Fig. 10) is an expression of second order equations.

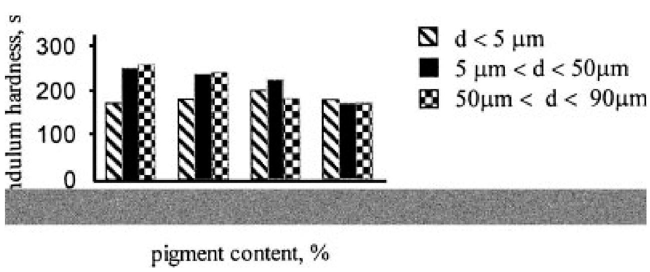

Figure 7 Pendulum hardness functions of green pigment particle size at different pigment content.

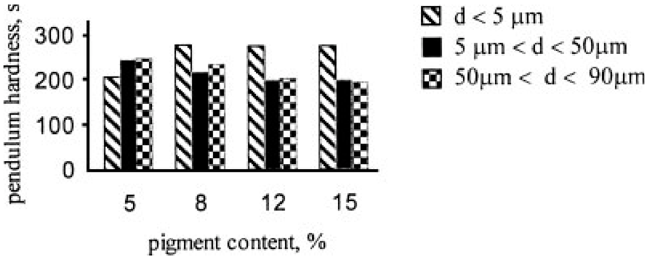

Figure 8 Pendulum hardness functions of blue pigment particle size at different pigment content.

For granulation greater than 50 μm, the extended dispersion of points does not allow a suitable correlation due to inadequate textural effect caused by higher granulation.

Although at granulation 50 μm $< d <$ 90 μm films, good mechanical properties were obtained, a granulation $d <$ 5 μm is used in practice because at this granulation the films have the best appearance, i.e., smooth and gloss. Small particle size distribution leads to a satin effect, while large particle size distribution leads to a sparkle effect.

Solvent resistance

Solvent rub technique (ASTM 5402) was used to assess the solvent (MEK) resistance of the UV-cured pigmented films. The results are presented in Table I.

Good results are obtained for blue pigmented films. The white pigment leads to lower solvent resistance.

Color measurements

Low content pigmented films present a certain degree of transparency. From this reason the measurements were carried out using two opaque backgrounds: white and colored standard corresponding to color.

Figure 11 depicts, for example, the brightness L—complementary parameter of color intensity—of red pigmented films as a function of pigment content at different granulations.

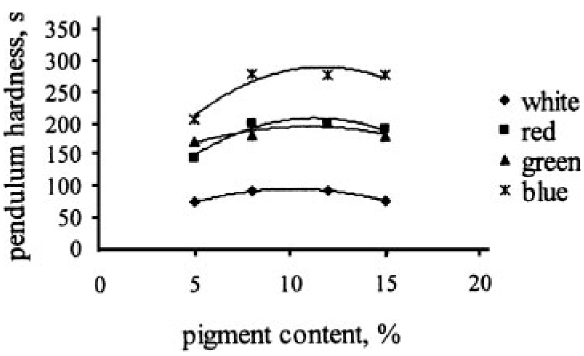

Figure 9 Dependence of film pendulum hardness on pigment content at a granulation $d <$ 5 μm.

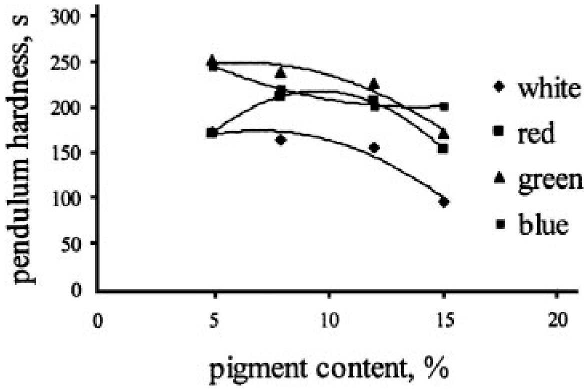

Figure 10 Dependence of film pendulum hardness on pigment content at a granulation 5 μm $< d <$ 50 μm.

The color brightness of red film samples decreases with the increase of pigment content. This parameter becomes important at granulation $d <$ 5 μm due to the homogeneity of monomer-pigment system. At a granulation $d >$ 5 μm, the contribution of the surface effect to the entire brightness is lower due to low homogeneity of the system. From this reason, it was established that a granulation $d <$ 5 μm is optimal for pigmented films.

The chromatic parameters, a and b (in HunterLAB system) were rectified by elimination of the background contribution and were calculated with eqs. (4) and (5):

$$a_r = a[1 - (Y - Y_{white})/Y] \quad (4)$$

$$b_r = b[1 - (Y - Y_{white})/Y] \quad (5)$$

where a_r and b_r are the parameters a and b rectified and Y_{white} is the experimental value determined using white background.

TABLE I
Solvent Resistance of the Films

Pigment ($d <$ 5 μm) color	Content (%)	MEK double rub resistance
White	5	138
	8	136
	12	134
	15	132
Red	5	146
	8	146
	12	144
	15	142
Green	5	158
	8	156
	12	156
	15	154
Blue	5	186
	8	186
	12	184
	15	184
Without pigment	–	198

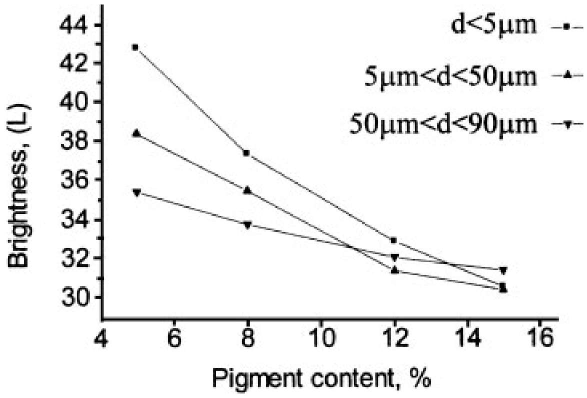

Figure 11 Brightness of red pigmented films.

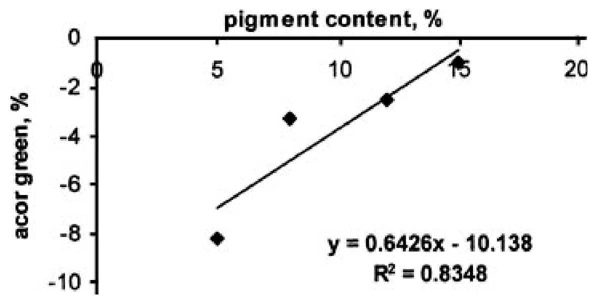

Figure 13 Green hue intensity ($-a$) of green film.

To characterize fairly and eloquently the pigmented films, those parameters from Hunter scale were selected corresponding to represented color

- Red color content for red films $+a$
- Blue color content for blue films $-b$
- Green color content for green films $-a$.

These parameters are useful to correlate the color intensity with the pigment content (at a constant granulation) or with mechanical properties (PH). In Figures 12–14 are represented a_r and b_r at granulation $d < 5$ μm, to obtain chromatic appearance in association with real color of the film, as a function of pigment content.

Figures 12–14 show a linear observed dependence between pigment content and chromatic appearance. In the case of red films, it was observed that the films containing 12 and 15% pigment have the close values of chromatic appearance, but in the first case the film has higher value of PH. In the case of green films, the similar situation appears when the films contain 8 and 12% pigment. The best chromatic appearance for blue film samples is obtained for 15% pigment content, because the hiding power of blue pigment is lower than red or green.

As a general rule, it can assert that these correlations can facilitate to find optimal condition for obtaining the acrylic colored films, related to desired characteristics: mechanical and chromatic. Also, these correlations can limit to minimize the number of experiments with economical advantages (reagents, energy and time consumption).

CONCLUSIONS

Photoinitiating system containing organophosphorus compound *p*-methoxybenzoyldiphenylphosphine oxide, previously synthesized, and 2,2-dimethoxy-2-phenylacetophenone was applied successfully to obtain pigmented acrylic films by UV exposure.

Inorganic pigments white, red, green, and blue at various size distribution d ($d < 5$ μm, 5 μm $< d <$ 50 μm and 50 μm $< d <$ 90 μm) and content (5–15%) were used to obtain acrylic colored films.

The mechanical characteristic (PH) and appearance (chromatic parameters) were correlated. The best results for PH were obtained for granulation 50 μm $< d <$ 90 μm and pigment content 5 and 8%. The best appearance (smooth glossy films) was obtained for granulation $d < 5$ μm and 8–15% pigment content. In this case, correlations among pigment content, PH, and chromatic parameters were established.

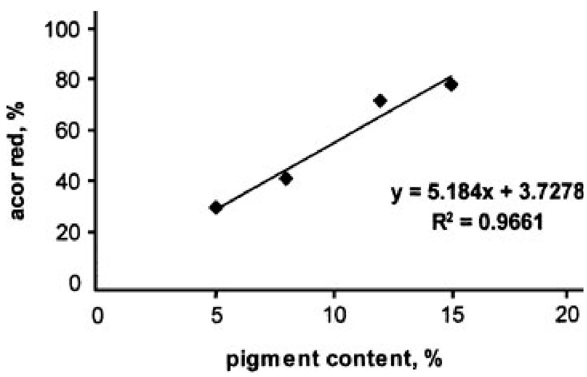

Figure 12 Red hue intensity ($+a$) of red film.

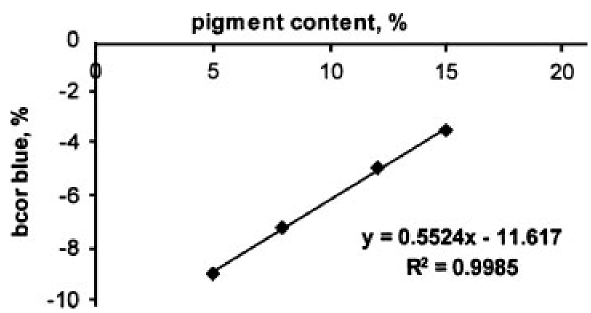

Figure 14 Blue hue intensity ($-b$) of blue film.

References

1. Lechtken, P.; Buethe, I.; Hesse A. (to BASF). Ger. Pat. DE 2,830,927 (1980).
2. Sumioshi, T.; Schnabel, W. Makromol Chemie 1985, 186, 1811.
3. Decker, C.; Zahouily, K.; Decker, D.; Nguyen, T.; Viet, T. Polymer 2001, 42, 7551.
4. Dietliker, K. K. In Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints, Vol. III: Photoinitiators for Free and Cationic Polymerisation; Oldring, P. K. T., Ed.; SITA Technology: London, 1991; p 173.
5. Rutsch, W.; Dietliker, K.; Leppard, D. G.; Koehler, M.; Misev, L.; Kolczak, U.; Rist, G. Progr Org Coat 1996, 27(1–4), 227.
6. Roffey, G. C. Photopolymerization of Surface Coatings; Wiley Interscience: London, 1982; p 17.
7. Fouassier, J.-P. Photoinitiation, Photopolymerization and Photocuring; Hanser Verlag: München, 1995.
8. Macarie, L.; Ilia, G.; Iliescu, S.; Popa, A.; Dehelean, G.; Manoviciu, I.; Petrean, A.; Abadie, M. J. M. Mol Cryst Liq Cryst 2004, 416, 165.
9. Baxter, J. E.; Davidson, R. S.; Hageman, H. J. Eur Polym J 1988, 24, 551.
10. Pierce, P. E.; Marcus, R. T. Color and Appearance; Federation of Societies for Coatings Technology: Blue Bell, PA, 1994.
11. Heine; Volz, H. G. Inorganic pigments. In Ullmann's Encyclopedia of Industrial Chemistry, 6th ed.; Wiley-VCH, Ed.; Wiley-VCH: Weinheim, 1998; Vol. 26.