

Transport of Blowing Agents in Polyurethane

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ABSTRACT: Desorption experiments are conducted for several blowing agents in polyurethane at room temperature and with various blowing agent pressures. The diffusivity and solubility data for blowing agents are compared with the corresponding values for chlorofluorocarbon 11 (CFC 11). In addition, the solubility and diffusivity for these blowing agents in polyurethane are explained in terms of the solubility parameter and van der Waals volume, respectively. The calculated permeabilities based on the measured diffusivities and solubilities indicate that among the nine blowing agents investigated in this study, eight blowing agents can be possible candidates for substitutes of CFC 11 in polyurethane foams. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 696–702, 2001

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INTRODUCTION

The possibility that the chlorine from chlorofluorocarbons (CFCs) could destroy the ozone layer in the stratosphere was advanced for the first time about 25 years ago by Rowland and Molina.¹ Since that time there was extensive scientific and political controversy over the fate of these chemicals. Recent observations of ozone depletion over the Arctic supported the hypothesis that the ozone loss is because of the photochemical process between chlorine and ozone.² Because CFCs are so stable, they can reach the ozone layer before being destroyed by natural processes. As a result, in 1992 the nations of the world agreed in Copenhagen to implement regulatory controls by ceas-

ing CFC production after 1995 in developed countries. Consequently, hydro-CFCs (HCFCs) were developed to replace CFCs. Although HCFCs still contain chlorine, they are more environmentally benign than CFCs because of the presence of carbon–hydrogen bonds that readily react in the lower atmosphere, significantly reducing the effect on the stratospheric ozone layer. HCFCs will be gradually phased out by 2030.

CFC 11 (CCl₃F) has been widely used in insulation foams because it is an easily handled liquid molecule that persists in the foam to maintain the foam's thermal resistance. However, the complete ban on CFC 11 and the proposed ban on its replacement HCFC 141b (CH₃CCl₂F) necessitate the search for alternative blowing agents that do not have ozone depletion potential. The desirable alternative blowing agents should produce foams having properties comparable to those made with CFC 11. During aging, the thermal resistance of insulating polymer foams decreases because of the counterdiffusion of the blowing agent and air. Therefore, information concerning loss of blowing

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agents from foams is a very important criterion in the selection of blowing agents. Models of blowing agent loss from insulating foams showed that this aging phenomena is a complex function of the blowing agent's diffusivity and solubility.^{3,4}

In a previous study⁵ the diffusivities and solubilities of CFC 11 and three HCFCs in polyurethane were measured at room temperature and with various blowing agent pressures. The calculated permeabilities based on the measured diffusivities and solubilities indicated that HCFC 142b (CH_3CClF_2) and HCFC 22 (CHClF_2) were possible candidates as substitutes for CFC 11 in polyurethane foams. This study measured the diffusivities and solubilities of several blowing agents without chlorine in polyurethane. The purpose of this work was to evaluate these possible candidates as blowing agents for rigid polyurethane insulating foams.

EXPERIMENTAL

Data Analysis

Diffusion Coefficient

If the diffusion coefficient is independent of concentration, the 1-dimensional diffusion process is generally described by the following expression:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where C is the penetrant concentration and D is the mutual diffusion coefficient. The solution of eq. (1) with appropriate initial and boundary conditions for a film of thickness $2l$ ($-l$ to l) exposed to an infinite reservoir of penetrants is given by⁶

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n + 1} \exp\left[\frac{-D(2n + 1)^2 \pi^2 t}{4l^2}\right] \cos\left[\frac{(2n + 1)\pi x}{2l}\right] \quad (2)$$

In sorption experiments the sorbed mass is obtained by integrating eq. (2) over the film thickness. At short times, if M_t denotes the total amount of penetrant that has diffused into the polymer sample at time t and M_∞ is the corresponding quantity at equilibrium, the following equation can be derived⁶:

$$\frac{M_t}{M_\infty} = \frac{2}{\sqrt{\pi}} \left(\frac{Dt}{l^2}\right)^{1/2} \quad (3)$$

Consequently, by plotting \sqrt{t} versus M_t/M_∞ , the diffusion coefficient can be determined from the initial slope of this relationship.

Solubility Coefficient

The solubility coefficient can be defined by Henry's law³:

$$S\left(\frac{\text{mol}}{\text{m}^3 \cdot \text{Pa}}\right) = \frac{n_{\text{sol}}}{V_{\text{pol}} P_{\text{sol}}} \quad (4)$$

where n_{sol} is the number of moles absorbed in the polymer, P_{sol} is the pressure of the penetrant at equilibrium, and V_{pol} is the volume of the polymer sample. In the literature, the solubility coefficient is often reported in milliliters of standard temperature and pressure (STP; 273.15 K and 1 atm) per milliliters of atmosphere ($\text{mL}_{\text{STP}}/\text{mL atm}$). In order to report data using this unit, a product of the gas constant (R) and the standard temperature (T_0 , 273.15 K) needs to be multiplied to the right side of eq. (4).

Permeation Coefficient

If a steady state has been reached and if Henry's law is valid, the permeation coefficient can be expressed as follows:

$$P = S \times D \quad (5)$$

In the literature, the permeation coefficient is usually reported in milliliters STP per centimeter seconds of centimeters of mercury ($\text{mL}_{\text{STP}}/\text{cm s cmHg}$).

Materials and Methods

Previous studies⁴ indicated that the diffusion coefficients for CFC 11 and other hydrocarbons in polyurethane at room temperature are very low. For example, a 0.02 cm thick polyurethane sample would take over 300 years to reach equilibrium if both sides of the sample were exposed to CFC 11. The duration time of such an experiment would be excessive even if a thin layer of polyurethane foam thick enough to be representative of the bulk foam was utilized. Because direct measurement of the blowing agent loss from rigid polyurethane foams is inhibited by the length of

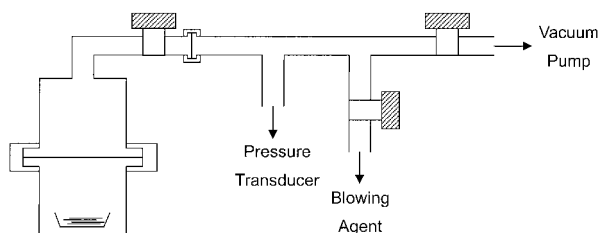


Figure 1 A schematic diagram of the desorption apparatus.

the experiments, an alternative approach was utilized to determine the diffusivity and solubility of blowing agents in very thin samples of bulk polyurethane. The available models were then used to correlate these data obtained from the bulk polymer to the effective diffusion through the foam. A microtome was used to produce very thin polyurethane samples so that experiments could be conducted over a reasonable period of time. A simple desorption experimental technique was developed that permitted measurements of the diffusivity and solubility of blowing agents in the thin polyurethane samples at ambient conditions. As compared to conventional gravimetric sorption experiments, the technique introduced in this study has the advantages of being simple and inexpensive and several experiments can be conducted simultaneously.

A schematic diagram of the apparatus used in this investigation is presented in Figure 1. It consisted of a glass reservoir formed by joining the upper and lower halves with a clamp and an O-ring seal. By a series of valves, this reservoir could be connected to a vacuum pump, a pressure transducer, and a blowing agent source. This apparatus consisted of two parts, the reservoir and the auxiliary apparatus, that could be used to serve several reservoirs. Before the experiment was initiated, the reservoirs were opened and a sample of the polyurethane was introduced. In a typical experiment, the polyurethane sample consisted of approximately 0.2 g of thin uniform slices of polyurethane contained in an aluminum screen bucket. The following experimental procedures were utilized:

1. The reservoir containing the aluminum bucket and the polyurethane samples was evacuated and kept under a vacuum for several days to remove materials such as water and air that may have been absorbed by the polyurethane.

2. The blowing agent vapor was introduced into the reservoir until the desired pressure was attained.
3. The reservoir was removed from the auxiliary filling apparatus and held in a constant temperature room for 2–3 weeks to permit equilibrium to be established between the blowing agent absorbed in the polyurethane and the blowing agent vapor.
4. After equilibrium was attained, the reservoir was reconnected to the auxiliary apparatus.
5. The auxiliary apparatus was evacuated and the valve on top of the reservoir was opened so that the pressure of the blowing agent could be determined with a pressure transducer.
6. The desorption experiment was initiated by evacuating the blowing agent in the reservoir and quickly replacing the blowing agent vapor with dry air so that the reservoir could be taken apart.
7. The bucket containing the polyurethane samples was quickly transferred to a conventional top-loading microbalance, which was housed in a box that was continuously purged with dry air. The weight of the bucket was measured over time.

Although some blowing agent was lost from the polyurethane samples before the first weight measurements were made, the linear relationship at early times between the amount of material absorbed as a function of the square root of time could be used to extrapolate the weight measurements back to time zero to determine the total amount of blowing agent in the polyurethane foam. This procedure was checked with duplicate experiments utilizing polyurethane samples of different thicknesses. The solubility of the blowing agent in the polyurethane was related to the mass of the blowing agent in the samples before the desorption experiment was initiated. The mutual binary diffusion coefficient for the blowing agent and polyurethane system was determined by the weight change during the early stages of the sorption process. The polyurethane samples were provided by Elf Atochem North America, Inc. in the form of approximately 0.25-in. diameter rods. The formulations of the polyurethane samples used in this study are provided in Table I. Uniform slices of polyurethane were cut from the rod using a microtome. Scanning electron microscope measurements indicated that the result-

Table I Polyurethane Formulation

Compound	Parts
Mondur MR (isocyanate index = 110)	78.2
Thanol R-310 ^a	100
PC-8/acetic acid (2/1 by moles)	0.3–0.5

^a A sorbitol based polyether polyol.

ing samples were fairly uniform in thickness and ranged from 6.4 to 7.4 μm . Similarly, the blowing agents were also provided by Elf Atochem North America, Inc.; the properties of these blowing agents⁷ are presented in Table II.

RESULTS AND DISCUSSION

The experimental results for the blowing agent and polyurethane systems are presented in Table III. In this table the P is the pressure of the blowing agent in the reservoir when equilibrium is attained between the polymer and the vapor phase. The activity of this system was determined by the ratio of the blowing agent pressure to the saturated vapor pressure of the pure blowing agent at the experimental temperature of 24°C, which was maintained in the constant temperature room during all the experiments. Table III also gives the measured solubility of the blowing agent in the polymer (S_{pol}), as well as the diffusivity and resulting permeability of the blowing agent in the polyurethane.

Figure 2 presents binary mutual diffusion coefficients of all the blowing agents in the polyure-

thane as a function of the weight percent blowing agent in the polymer. This figure indicates that the binary mutual diffusion coefficients of various blowing agents are a strong function of the blowing agent concentration in the polymer. In polymer/solvent systems, solvents swell polymers and increase their mobility, and hence their diffusivity in the polymer.⁸ In addition to the effect of solvent concentration, diffusion of solvents in polymers is also influenced by the molecular size of the solvent. Figure 2 presents the diffusivity data for blowing agents having van der Waals volume values lower than 4×10^{-2} (m^3/kmol) and those having values higher than 4×10^{-2} (m^3/kmol). Specific values for all the blowing agents are provided in Table II. Consequently, as shown in Figure 2, HFC 134a, HFC 143a, and HFC 152a diffuse quicker than the other blowing agents; this agrees with the size of the solvents as listed in Table II. The only exception in this study is the n -pentane. It is known that n -pentane migrates segmentally.^{9–11} Therefore, although the van der Waals volume of n -pentane is the highest among the blowing agents investigated in this study, its diffusivity is higher than the other blowing agents as shown in Figure 2. Diffusivity data for CFC 11 are also provided for comparison. Experimental studies and theoretical descriptions of solvent diffusion in polymers⁸ indicate that not only will larger molecules diffuse more slowly, but also the concentration dependency of the diffusivity is more pronounced for larger solvent molecules. Consequently, it can be anticipated that the larger blowing agents included in Figure 2 such as CFC 11 will show a precipitous drop in the

Table II Properties of Blowing Agents

	Formula	Molecular Weight	Boiling Point (°C)	Solubility Parameter (cal/mL) ^{1/2}	van der Waals Volume (m^3/kmol)
CFC 11	CCl_3F	137.38	24	7.617	4.605×10^{-2}
HFC 245fa	$\text{CHF}_2\text{CH}_2\text{CF}_3$	134.06	15	NA	NA
HFC 245ca	$\text{CH}_2\text{FCF}_2\text{CHF}_2$	134.06	25	NA	NA
HFC 245eb	$\text{CH}_2\text{FCHF}_2\text{CF}_3$	134.06	23	NA	NA
HFC 365mfc	$\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_3$	148.08	40	NA	NA
Cyclopentane	C_5H_{10}	70.14	50	8.091	4.969×10^{-2}
n -Pentane	C_5H_{12}	72.15	35	7.040	5.803×10^{-2}
HFC 134a	CHF_2CHF_2	102.04	-26	8.067	3.756×10^{-2}
HFC 143a	CH_3CF_3	84.05	-47	7.592	3.500×10^{-2}
HFC 152a	CH_3CHF_2	66.05	-24	8.521	3.245×10^{-2}

Table III Results for Polyurethane/Blowing Agent Systems at Room Temperature

Blowing Agent	P (psi)	Activity	wt %	$S_{\text{pol}}RT_0$ (mL _{STP} /mL atm)	$D_{\text{pol}} \times 10^{12}$ (cm ² /s)	$P_{\text{pol}} \times 10^{12}$ (mL _{STP} /cm s cmHg)
HFC 245fa	8.0	0.389	5.4	20.22	2.8	0.74
HFC 245ca	10.0	0.735	7.1	20.90	6.9	1.90
	6.2	0.439	2.7	12.68	1.2	0.20
HFC 245eb	9.3	0.608	8.5	28.60	6.0	2.26
	6.0	0.392	3.7	18.00	3.9	0.92
HFC 365mfc	7.0	0.891	5.4	21.08	4.4	1.22
	6.8	0.841	5.5	22.04	3.2	0.93
Cyclopentane	5.7	0.963	4.2	41.99	5.1	2.82
	4.2	0.740	4.0	53.60	4.6	3.20
<i>n</i> -Pentane	8.7	0.909	3.3	19.91	6.9	1.81
	4.5	0.470	1.6	19.25	3.4	0.86
HFC 134a	13.7	0.165	1.7	4.84	8.1	0.52
	12.8	0.154	1.5	4.40	4.6	0.27
	9.6	0.116	1.2	4.62	1.7	0.10
HFC 143a	13.0	0.090	1.3	4.64	9.3	0.57
	9.6	0.064	1.1	5.46	3.7	0.27
HFC 152a	14.0	0.165	2.3	9.84	17.4	2.25
	10.8	0.127	1.7	9.33	9.9	1.22

diffusivity as the solvent concentration is reduced. For example, CFC 11 has a measured diffusivity of approximately 1×10^{-12} (cm²/s) at 4 wt %, and this value may drop several orders of magnitude for CFC diffusion at concentrations below 1 wt %.

The experimental results for all the blowing agents in terms of the weight percent blowing agent in the polyurethane as a function of the blowing agent activity are presented in Figure 3. In this figure the solubility data for CFC 11 are also provided for comparison, and the the linear regression of these data are represented. Thermodynamic theories for polymer/solvent systems would indicate that species with similar solubility parameters would have equivalent solubilities in a given polymer when the solubility in terms of the weight fraction or volume fraction is considered at a given solvent activity. The values of the solubility parameters for the blowing agents are provided in Table II. Solubility parameters for HFC 245 and HFC 365mfc are not available in the literature. A comparison of the data presented in Figure 3 and the corresponding solubility parameters for the blowing agents shows that there is not a good correlation between the measured solubilities and the solubility parameters. Others showed the limitations of using solubility parameters as indicators of solubility, particularly for polar and hydrogen bonding systems.¹²

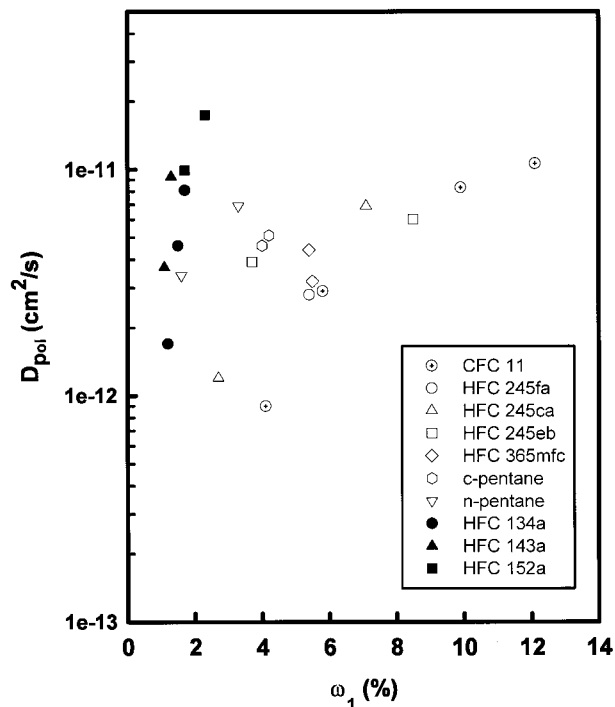


Figure 2 The diffusivity data for blowing agent and polyurethane systems at 24°C. The mutual binary diffusion coefficients are presented as a function of the weight percent of blowing agent in the polymer. The solid symbols correspond to the diffusivity data for blowing agents having van der Waals volume values lower than 4×10^{-2} (m³/kmol) whereas the open symbols represent blowing agents having values higher than 4×10^{-2} (m³/kmol).

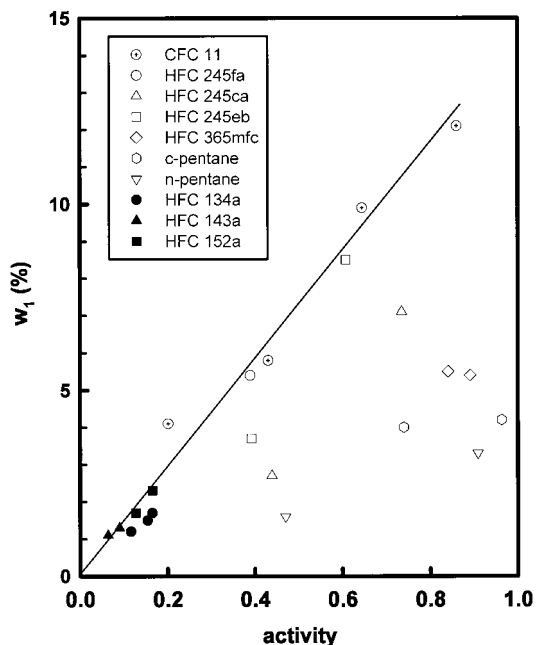


Figure 3 The solubility data for blowing agent and polyurethane systems at 24°C. The results are expressed as the weight percent of blowing agent in the polymer as a function of the activity of the blowing agent. (—) The linear regression of the solubility data for CFC 11.

Figure 4 presents the permeabilities of the blowing agents in polyurethane as a function of pressure. The permeability data for CFC 11 are also provided for comparison, and the linear regression of these data are represented. Because the total pressure within the cells of a freshly blown polyurethane foam is typically between 10 and 13 psi (including gaseous CO₂ from the water-isocyanate reaction), the permeability at these pressures would be the relevant information for determining how quickly the blowing agent will start to leave the foam. As shown in Figure 4, the permeability decreases for all the blowing agents as the amount of blowing agent in the foam decreases.

As mentioned before, during aging of insulation foams, the thermal resistance of the foams decreases because of the counterdiffusion of the blowing agent and air. Therefore, information concerning the loss of blowing agents from foams is a very important criterion in the selection of blowing agents. Models of blowing agent transport in rigid insulating foams indicate that an effective diffusion coefficient (D_{eff}) for the transport of the blowing agent through the foam can be estimated from the solubility and diffusivity of

the blowing agent in the polymer phase of the foam.⁴ Such models indicate that the ratio of D_{eff} for two blowing agents can be determined by the following expression:

$$\frac{D_{\text{eff},1}}{D_{\text{eff},2}} = \frac{D_{\text{pol},1}S_{\text{pol},1}}{D_{\text{pol},2}S_{\text{pol},2}} \times \frac{f_g + (1 - f_g)S_{\text{pol},2}RT}{f_g + (1 - f_g)S_{\text{pol},1}RT} \quad (6)$$

where f_g is the void volume fraction of the foam. Because the value of f_g is very close to 1.0 for most foams, the second term of the right side of eq. (6) is generally close to 1.0. Therefore, as a first approximation, the ratio of the effective diffusivities for two blowing agents is equivalent to the ratio of the two permeabilities.

Based on this analysis, Figure 4 indicates that all the blowing agents studied (except cyclopentane) would be good candidates as substitutes for CFC 11. Although the diffusion coefficients of HFC 134a, HFC 143a, and HFC 152a are the highest among the blowing agents investigated in this study, because of their low solubility coefficients, the permeabilities of these blowing agents are lower than other blowing agents at pressures between 10 and 13 psi. Of course, other properties of blowing agents in addition to the permeability are important in this application such as the ther-

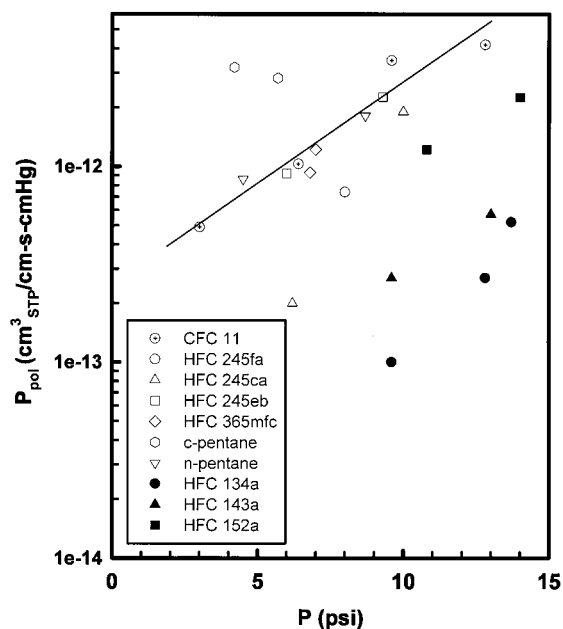


Figure 4 The permeability data for the blowing agent and polyurethane systems at 24°C. The calculated permeabilities are presented as a function of the blowing agent pressure in the polymer. (—) The linear regression of the permeability data for CFC 11.

mal conductivity of the blowing agent vapor in the foam and the interaction of the blowing agent with ozone.

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REFERENCES

1. Molina, M. J.; Rowland, F. S. *Nature* 1974, 249, 810.
2. von der Gathen, P.; Rex, M.; Harris, N. R. P.; Lucic, D.; Knudsen, B. M.; Braathen, G. O.; Backer, H. D.; Fabian, R.; Fast, H.; Gil, M.; Kyrö, E.; Mikkelsen, I. S.; Rummukainen, M.; Stähelin, J.; Varotsos, C. *Nature* 1995, 375, 131.
3. Brodt, K. H.; Bart, G. C. J. *J Cell Plast* 1993, 29, 478.
4. Bart, G. C. J.; du Cauz de Nazelle, G. M. R. *J Cell Plast* 1993, 29, 29.
5. Hong, S. U.; Duda, J. L. *J Appl Polym Sci* 1998, 70, 2069.
6. Crank, J. *The Mathematics of Diffusion*; Oxford University Press: New York, 1975; 2nd ed.
7. Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Compounds, Data Compilation*; Taylor and Francis: New York, 1997.
8. Duda, J. L.; Zielinski, J. M. In *Diffusion in Polymers*; Neogi, P., Ed.; Marcel Dekker: New York, 1996; Chapter 3.
9. Vrentas, J. S.; Duda, J. L. *J Polym Sci Polym Phys Ed* 1979, 17, 1085.
10. Vrentas, J. S.; Liu, H. T.; Duda, J. L. *J Appl Polym Sci* 1980, 25, 1793.
11. Vrentas, J. S.; Duda, J. L.; Hou, A. C. *J Appl Polym Sci* 1980, 25, 1793.
12. van Krevelen, D. W. *Properties of Polymers*; Elsevier Science: Amsterdam, 1990; 3rd ed.