Vol. 9, No. 1, pp. 6-11, June 2010

INTERNATIONAL JOURNAL OF SAFETY
www.kosos.or.kr

Thermal Hazard Evaluation on Self-polymerization of MDI

Yoshihiko Sato*, Ken Okada, Miyako Akiyoshi, Satoshi Murayama[1] and Takehiro Matsunaga

Research Institute of Science for Safety and Sustainability, National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, 305-8565, Japan
[1]Central Research Laboratory, Nippon Polyurethane Industry Co., Ltd., Akiba-Cho 440, Totsuka-Ku Yokohama 245-0052, Japan

(Received; February 3, 2010; Accepted June 10, 2010)

Abstract : Thermal analysis, heating test on gram scale and simulation of exothermic behavior based on kinetic analysis has been conducted in order to evaluate thermal hazards of self-polymerization of MDI. The exothermic reactions of MDI are expected to be the polymerization which forms carbodiimide and carbon dioxide, dimerization and trimerization. When MDI is kept in adiabatic condition during 1 week (10080 hours), the simulated result shows runaway reaction can occur in the case that initial temperature was more than 130°C. The relationship between the initial temperature (T, °C) and TMR is given in a following equation.

$TMR = 4.493 \times 10^{-7} \exp (9.532 \times 10^{3}/(T+273.15))$

We propose that the relationship gives important criteria of handling temperature of MDI to prevent a runaway reaction.

Key words: MDI (diphenylmethane diisocyanate), self-polymerization, thermal hazard, thermal analysis, simulation

1. Introduction

Diphenylmethane diisocyanate (MDI) is the most important material of polyurethane because of high reactivity and ease in handling. Isocyanate reacts with nucleophile, such as water, to exotherm and to form carbon dioxide [1]. It has been known that the reaction of isocyanate was one of causes of release accident of toxic gas in Bhopal [2]. Accordingly the reaction of isocyanate is generally recognized as a hazard factor in handling of isocyanate. On the other hand, aromatic isocyanate, such as MDI, polymerizes itself and generates polymeric carbodiimide and carbon dioxide at about 300°C [3]. Though self-polymerization of isocyanate in high temperature and reaction between isocyanate and nucleophile are identical in generating of heat and carbon oxide, self-polymerization of isocyanate is not recognized enough as a hazard factor. Depending on handling condition, internal pressure in MDI tank arises and explosion accidents may occur. An explosion accident of MDI tank actually occurred in Japan. Therefore it is important for prevention of explosion accidents to comprehend quantitatively progress of self-polymerization of MDI. The purpose of this study is to evaluate reaction hazards in self-polymerization of MDI. Heat of reaction and generating gas was analyzed by thermal analysis. A heating test on gram scale has been carried out in order to verify that self-polymerization of MDI caused explosion phenomena. Based on the scanning results with thermal analysis using several differing scanning rates, kinetic parameters of MDI reactions have been estimated. Based on the obtained kinetic parameters, the exothermic behavior of MDI in heating condition has been simulated. The simulated result has been compared with the heating test on gram scale. Moreover, the exothermic behavior in the adiabatic condition as the most conservative condition has been simulated.

*Corresponding author: yoshihiko-satou@aist.go.jp

2. Experiment

2.1 Materials

Polymethylene polyphenyl polyisocyanate (Nippon Polyurethane Industry Co. Ltd., purity: more than 99 %) has been used as MDI in this study.

2.2 Thermal analysis

Differential scanning calorimeter (DSC) has been used for analyzing heat of reaction and kinetic parameters. In this study, the samples heat in SUS sealed cells up to 500°C with heating rates of 2, 5, 10 and 20 K min^{-1} in 0.1 MPa nitrogen atmosphere.

2.3. Heating test on gram scale

MDI is poured in 200 mL sealed glass vessel. The thickness of the vessel was 2.4 mm. The amount of MDI was 70 g. the vessel is heated by the handmade adiabatic furnace. Figure 1 shows a schematic diagram of the adiabatic furnace. Thermal insulator is filled in enameled vessel (250 mm^f×250 mm^h) and stainless vessel (80 mm^f×180 mm^h, 5 mm^t, 904 mL) is set in the enameled vessel. Thermal insulator (130 mm^h) is filled to the bottom of the stainless vessel to prevent direct heat transfer from the vessel. Flexible heater (16 mm^f× 1700 mm^L, 100 VAC, 500 W) is twisted spirally on the surface of the stainless vessel. Two thermocouples are set on the side of the stainless vessel and one of the thermocouple is connected to temperature controller (CHINO KP1000) that controlled temperature of the adiabatic furnace. Temperature (temperature of the surface of the adiabatic furnace No. 1, No. 2, temperature in the furnace and room temperature) is measured by sheath thermo-couples (1.6 mm^f, K type) and records by data logger (OMRON, ZR-RX40). The sample is observed using a video camera during the heating tests. The adiabatic furnace is heated from room temperature with heating rate of 10 K min^{-1} and is kept at 420°C finally.

3. Simulations

3.1 Kinetic analysis and non-linear regression

NETZSCH kinetic software [4] has been used for kinetic analysis and multivariate non-linear regression. A series of dynamic scans with different heating rates results in a set of data, which exhibits the same degree of conversion at different temperatures. Based on this, kinetic parameters (activation energy and pre-exponential factor) has been roughly evaluated by Friedman method [5] and Ozawa-Flynn-Wall method [6, 7] using the DSC experimental data. Based on these kinetic parameters, reaction paths and mechanism functions have been assumed and multivariate non-linear regression has been applied to the DSC experimental results.

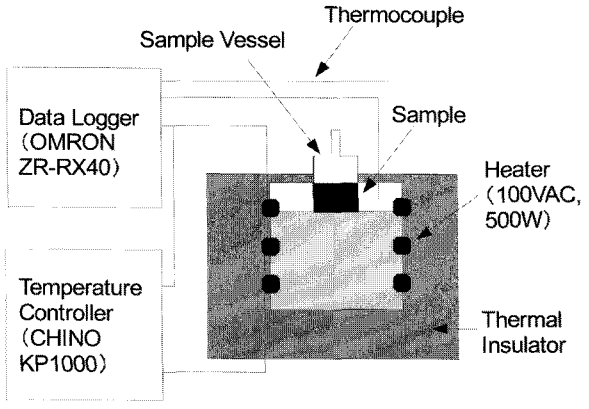


Fig. 1. Schematic diagram of the handmade adiabatic furnace.

3.2 Simulation of exothermic behavior

Based on the evaluated reaction model, exothermic behavior of MDI in adiabatic condition has been simulated. NETZSCH thermal simulations software [8] has been used in the simulation. A following expanded form of the Thomas model [9] is used to characterize the exothermic behavior in the software.

$$\lambda\left(\frac{\partial^2 T}{\partial r^2}+\frac{j}{r}\frac{\partial T}{\partial r}\right)+\rho \bullet C_v \bullet \frac{\partial T}{\partial t}=(-\Delta H)\bullet f(c,t,T)$$

where λ is thermal conductivity, r is radial distance from the center, j is a geometry factor which is dependent on the type of reactor ($j=0$ for the infinite plate, $j=1$ for the infinite cylinder, $j=2$ for the sphere), ρ is density of the reactants, c_v is specific heat, ΔH is the heat of reaction and $f(c,t,T)$ is the function of heat generation. The evaluated reaction model has been substituted for this function of heat generation.

The simulated result and the experimental data of heating test on gram scale have been compared. Exothermic behavior of MDI in adiabatic condition has been simulated. Initial temperature has varied from 12°C to 220°C.

4. Results and discussion

4.1 Kinetic analysis and non-linear regression for the thermal analysis data

Figure 2 shows the DSC charts of MDI. Table 1 shows measured peak temperature and heat of reaction of MDI. Three exothermic peaks have been observed in the DSC charts. For example, exothermic peaks have been observed at 257°C, 339°C and 441°C in the case of heating rate of 10 K min^{-1}. This result shows that at least three exothermic reactions occur apparently. The exothermic peaks shift to higher temperature when heating rate increases. The degree of shift has been different at each peak. This phenomenon shows that reaction rates of each exothermic reaction are different.

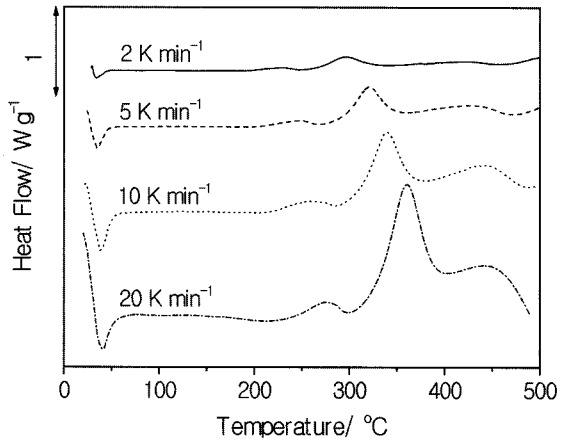


Fig. 2. DSC charts of MDI at heating rate of 2, 5, 10 and 20 K min^{-1}.

Table 1. Measured peak temperature (T_{MAX}) and heat of reaction (Q_{DSC}) of MDI using DSC

Heating Rate/ K min^{-1}	T_{MAX}/°C			Q_{DSC}/ J g^{-1}
	1st Peak	2nd Peak	3rd Peak	
2	228	296	422	285
5	245	322	427	313
10	257	339	441	333
20	275	360	443	347

Figure 3 and 4 shows the estimated activation energy and pre-exponential factor using Friedman method and Ozawa-Flynn-Wall method, respectively. The activation energy and pre-exponential factor is not a constant value at each degree of conversion (a). Therefore, the reaction is not a single step reaction at least. It appears that the estimated activation energy has been divided into three regions ($\alpha < 0.1$, $0.1 < \alpha < 0.6$ and $0.6 < \alpha$).

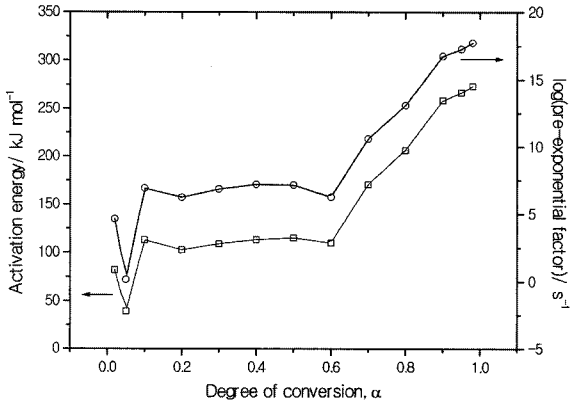


Fig. 3. Activation energy and pre-exponential factor estimated by Friedman method.

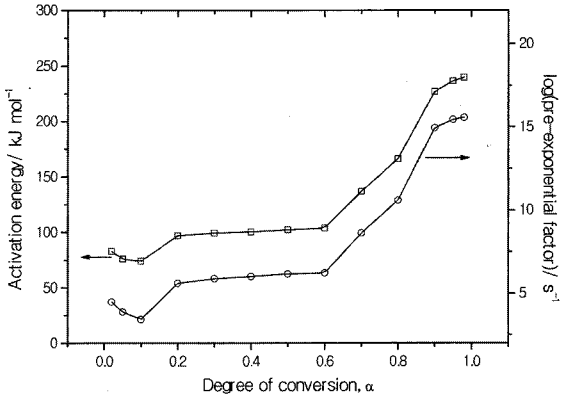


Fig. 4. Activation energy and pre-exponential factor estimated by Ozawa-Flynn-Wall method.

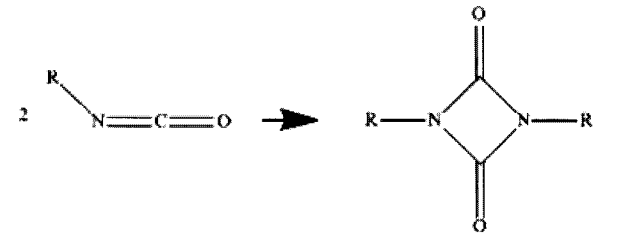
The activation energy has been almost equal in the region of $0.1 < \alpha < 0.6$. This reaction in the region of $0.1 < \alpha < 0.6$ is highly probable to be a single reaction. On the other hand, the activation energy has been not equal in the region of $\alpha < 0.1$ and $0.6 < \alpha$. This fact suggests that the reaction which is difficult to estimate activation energies using model-free analysis (such as a competitive reaction) occurs in the region of degree of

Table 2. Type of reaction and reaction equation

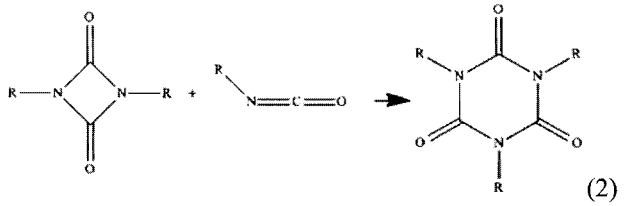
Type of reaction	Reaction equation
First-order reaction	$(1-\alpha)$
Second-order reaction	$(1-\alpha)^2$
n^{th}-order reaction	$(1-\alpha)^n$
One-dimensional diffusion	$0.5\alpha^{-1}$
Two-dimensional diffusion	$(-\ln(1-\alpha))^{-1}$
Three-dimensional Jander's diffusion	$1.5(1-\alpha)^{1/3}/[(1-\alpha)^{-1/3}-1]$
Three-dimensional Ginstling-Brounshtein diffusion	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
Two-dimensional phase boundary reaction	$2(1-\alpha)^{1/2}$
Three-dimensional phase boundary reaction	$3(1-\alpha)^{2/3}$
Autocatalytic reaction, according to Prout-Tompkins equation	$\alpha(1-\alpha)$
a^{th}-degree autocatalytic reaction with an n^{th}-order reaction Prout-Tompkins equation	$\alpha^n(1-\alpha)^a$
First-order reaction with autocatalysis	$(1-\alpha)(1+k\text{-cat}\alpha)$
n^{th}-order reaction with autocatalysis	$(1-\alpha)^n(1+k\text{-cat}\alpha)$
Two-dimensional nucleation, Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
Three-dimensional nucleation, Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
n-demensional nucleation, Avrami-Erofeev	$n(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$

conversion.

MDIpolymerizes itself and generates polymeric carbodiimide and carbon dioxide at high temperature. Moreover, MDI dimerizes and trimerizes and form uretdione and isocyanurate as following reaction formula Eq. (1) and (2) [3]. Thus it is reasonable to suppose that the above exothermic peaks show the polymerization which forms carbodiimide and carbon dioxide, dimerization and trimerization.

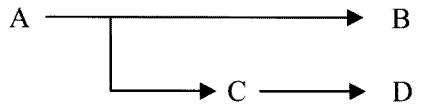


(1)



(2)

Based on these reactions, the following three-step model is assumed.



We have assumed that the reaction of A to B is the polymerization which forms carbodiimide and carbon dioxide, and the reactions of A to C and C to D are dimerization and trimerization of MDI, respectively. The type of reaction shown in Table 2 has been applied to each reaction, and the best type of reaction to explain the experimental DSC data has been searched.

Figure 5 shows the experimental DSC data and the result of multivariate non-linear regression. Table 3 shows the estimated kinetic parameters by multivariate non-linear regression. This model consists of 1st order reaction of auto-catalysis (from A to B) and n^{th} order reactions (from A to C and from C to D). The result of regression is similar to the experimental results.

3.3.2 Simulation of exothermic behavior

The exothermic behavior of MDI in the heating test on gram scale has been simulated using the estimated reaction type and kinetic parameters. The simulated

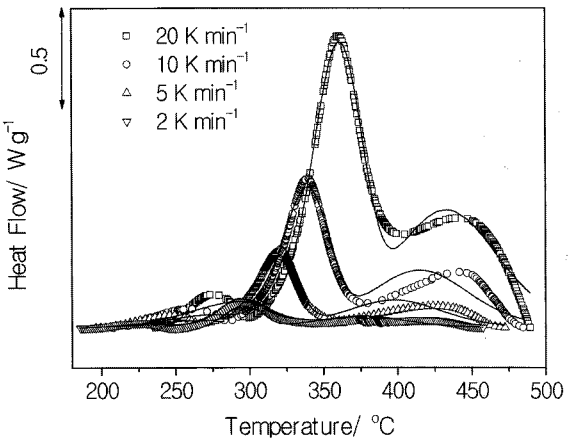


Fig. 5. The experimental DSC data and simulated results by multivariate non-linear regression (dot: experimental data, line: simulated results).

Table 3. Estimated kinetic parameters by multivariate non-linear regression

Parameter	Optimum value	Standard deviation
Log A1/ s^{-1}	5.3649	2.3117
E1/ kJ mol^{-1}	93.6845	1.1938
Log Kcat1	-0.2812	1.9903
Log A2/ s^{-1}	6.0552	0.5521
E2/ kJ mol^{-1}	93.6382	1.1805
React. Ord. 2	0.9454	0.0458
Log A3/ s^{-1}	8.7003	0.8215
E3/ kJ mol^{-1}	143.4273	10.4703
React. Ord. 3	1.5988	0.1257
CompReact. 1	-148.8310	954.2009
CompTotal2+3	30.9901	10.1678
FollReact. 2	0.9816	0.0175
Area 1/ J g^{-1}	338.3494	Constant
Area 2/ J g^{-1}	315.9074	Constant
Area 3/ J g^{-1}	295.1180	Constant
Area 4/ J g^{-1}	288.1567	Constant

result and the experimental data of heating test on gram scale have been compared. The following parameters have been assumed: thermal conductivity, λ is 1.4×10^{-4} W cm^{-2} K^{-1}, radial distance, r is 4 cm, specific heat, c_v is 2.04 J g^{-1} K^{-1}, density, r is 1.22 g cm^{-3}. Thermal conductivity, density of the reactants and specific heat are literature data. Radial distance, geometry factor, heat of reaction and the surface heat transfer coefficient are experimental data.

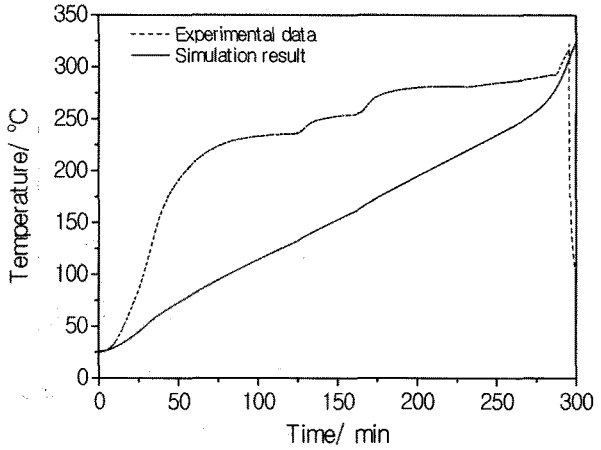


Fig. 6. The experimental data of temperature in the adiabatic furnace in the heating test on gram scale and the simulated result of temperature of MDI.

Figure 6 shows the experimental data of temperature in the adiabatic furnace in the heating test on gram scale and the simulated result of temperature of MDI. The simulated temperature of MDI is not in agreement with the experimental data of temperature in the adiabatic furnace. The measured temperature is temperature inside the furnace. That is to say sample temperature is not directly measured. For this reason, absolute value of temperature is not simply compared. On the other hand, time to runaway reaction in the heating test on gram scale is almost equal to that of the simulated result. The fact that time to runaway reaction is almost equal suggests that reaction rate up to runaway is almost equal. Accordingly exothermic behavior of MDI in the case of scale up can be predicted by this simulation.

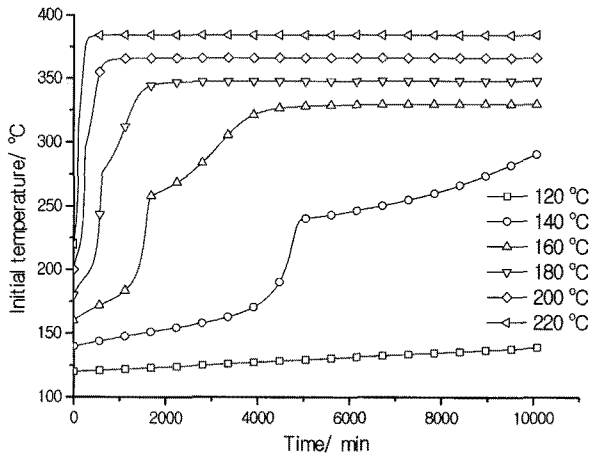


Fig. 7. Simulated exothermic behavior of MDI in adiabatic condition.

Table 4. The estimated TMR at each initial temperature

Initial temperature/°C	TMR/ min
130	8624
140	4788
150	2716
160	1596
170	952
180	588
190	364
200	280
210	168
220	112

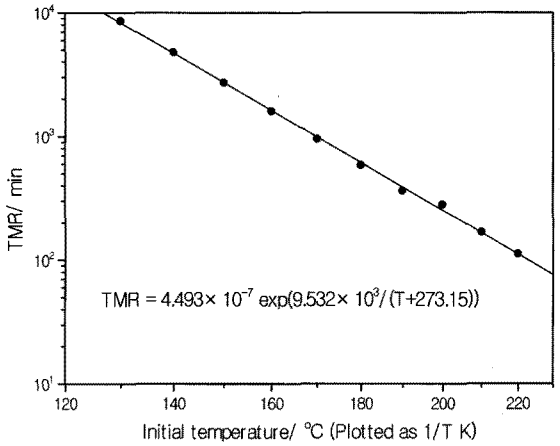


Fig. 8. The relationship between initial temperature and TMR.

Exothermic behavior of MDI in adiabatic condition has been simulated. Initial temperature varies from 120°C to 220°C Figure 7 shows the simulated exothermic behavior of MDI in adiabatic condition. When MDI is kept in adiabatic condition during 1 week (10080 hours), the simulated result shows runaway reaction can occur in the case that initial temperature was more than 130°C.

Table 4 shows the estimated time to maximum heat rate (TMR) at each initial temperature. Fig. 8 shows the relationship between initial temperature and TMR. The logarithm of TMR is proportional to the reciprocal of the absolute temperature of initial temperature.

The relationship between the initial temperature (T, °C) and TMR is given in a following equation.

$$TMR = 4.493\times10^{-7} \exp\left(9.532\times10^{3}/(T+273.15)\right)$$

We propose that this relationship gives important criteria of handling temperature of MDI to prevent a runaway reaction.

4. Conclusions

In order to evaluate thermal hazards of self-polymerization of MDI, thermal analysis, heating test on gram scale and simulation of exothermic behavior based on kinetic analysis have been conducted and following conclusions can be drawn.

- The exothermic reactions of MDI are expected to be the polymerization which forms carbodiimide and carbon dioxide, dimerization and trimerization.
- When MDI is kept in adiabatic condition during 1 week (10080 hours), the simulated result shows runaway reaction can occur in the case that initial temperature was more than 130°C.
- The logarithm of TMR is proportional to the reciprocal of the absolute temperature of initial temperature. We propose that the relationship gives important criteria of handling temperature of MDI to prevent a runaway reaction.

References

[1] P. G. Urban (Ed.), *Bretherick's handbook of reactive chemical hazards, 7th ed. vol. 2*, Amsterdam: Elsevier, 2007.

[2] F. P. Lees, *Loss prevention in the process industries, 2nd ed. Vol. 3*, Oxford: Butterworth-Heinemann, 1996.

[3] H. J. Saunders and K. C. Frisch, *High polymers vol. 16 pt. 1, Polyurethanes: Chemistry and technology*, New York: Interscience, 1962.

[4] NETZSCH-Gerätebau GmbH, NETZSCH Thermokinetics software, Version 2002.1a.

[5] H. L. Freidman, "Kinetics of thermal degradation of char-forming plastics from thermogravimetry – application to a phenolic plastic", *J. Polym. Sci. C*, Vol. 6, p. 183, 1964.

[6] T. Ozawa, "A new method of analyzing thermogravimetric data", *Bull. Chem. Soc. Japan*, Vol. 38, No. 11, pp. 1881-1886, 1965.

[7] J. Flynn and L. A. Wall, "A quick direct method for the determination of activation energy from thermogravimetric data", *J. Polym. Sci. B Polym. Lett.*, Vol. 4, p. 323, 1966.

[8] NETZSCH-Gerätebau GmbH, NETZSCH Thermal Simulations software, Version 2002.02a.

[9] P. H. Thomas, "On the thermal conduction equation for self-heating materials with surface cooling", *Trans. Faraday Soc.*, Vol. 54, pp. 60-65, 1958.