MARIUSZ B. BOGACKI, EWA ANDRZEJEWSKA,
MACIEJ ANDRZEJEWSKI
Poznań University of Technology
Institute of Chemical Technology and Engineering
Pl. Skłodowskiej-Curie 2, 60-965 Poznań
e-mail: Ewa.Andrzejewska@put.poznan.pl

Modeling the polymerization kinetics of a dimethacrylate monomer in the after-effect period

RAPID COMMUNICATION

Summary — Isothermal differential scanning photocalorimetry was used to monitor the light-induced (366 nm; 1.3 mW/cm^2; 40°C, Ar atm.) polymerization of (diethylene glycol) dimethacrylate proceeding in the presence of 0.03 M 2,2-dimethoxy-2-phenylacetophenone and to study variations in the mechanism of termination in the after-effect period after illumination had been discontinued. Illumination was stopped at five moments of the reaction corresponding to different degrees of double bond conversion. Three termination models, mono [I, eq. (1)], bimolecular [II, eq. (2)], and mixed type [III, eq. (3)], were used to evaluate parameters k_t^{m} and $k_p[P^·]_0$; $k_t^{b}[P^·]_0$ and $k_p[P^·]_0$; and k_t^{m}, $k_t^{b}[P^·]_0$ and $k_p[P^·]_0$, resp., where k_t^{m} and k_t^{b} are the mono and the bimolecular termination rate coefficients, k_p is the propagation rate coefficient and $[P^·]_0$ is the macroradical concentration at the start of the dark reaction. The parameters were calculated at various durations of postpolymerization (10—160 s at 10-s increments) starting invariably at the moment of discontinuation of illumination. In this manner, the propagation and termination rate coefficients were averaged over increasingly large dark conversions. Two-stage statistical analysis was used to find the "best" model. Termination was found to follow the mechanism varying with time of dark reaction from the bimolecular to the mixed type, whereby radical trapping is seen to be increasingly important. Model III was the only model to describe correctly the variation of the dark reaction rate coefficients with time, *i.e.*, the increase in k_t^{m} and decrease in the product $k_t^{b}[P^·]_0$.

Key words: termination mechanism, after-effect, modeling, postpolymerization rate coefficients, dimethacrylate.

The kinetics of photoinitiated polymerization of multi(meth)acrylates is complicated by some factors that are not observed in linear polymerization. The exceptional polymerization behavior can mostly be attributed to diffusional limitations of the mobility of the reacting species. In a bulk crosslinking polymerization they exist from the onset of the reaction [1].

Radicals connected to the network tend to get trapped. Trapped radicals are surrounded by "dead" polymer chains and are inaccessible for the further reaction. Thus, in the polymerizing medium there coexist two dominant populations of radicals with different reaction tendencies: free radicals the mobility of which is not directly restricted by spatial constraint and trapped radicals. This leads to two types of termination reaction: the usual bimolecular interaction of polymer radicals (bimolecular termination) characterized by bimolecular termination rate coefficient k_t^{b} and the first-order process involving only one polymer radical (monomolecular termination) characterized by monomolecular termination rate coefficient k_t^{m}. Therefore, the termination process may be considered to occur according to one of three possible termination mechanisms: *monomolecular*, *bimolecular* and *mixed* [2—5]. In the absence of initiation the postpolymerization can be described by three *termination models* [2, 4, 5]:

the *monomolecular* termination model (model I):

$$-\ln(1-p_d) = \frac{k_p}{k_t^m} [P^*]_0 (1-\exp(-k_t^m t))$$ (1)

the *bimolecular* termination model (model II):

$$-\ln(1-p_d) = \frac{1}{2} \cdot \frac{k_p}{k_t^b} \ln(1 + 2 \cdot [P^*]_0 \cdot k_t^b \cdot t)$$ (2)

the *mixed* termination model (model III):

$$-\ln(1-p_d) = \frac{1}{2} \cdot \frac{k_p}{k_t^b} \ln\{1 + 2 \cdot [P^*]_0 \cdot \frac{k_t^b}{k_t^m} (1-\exp(-k_t^m t))\}$$ (3)

where k_p is the *propagation rate coefficient*, $[P^*]_0$ is the *macroradical concentration at the beginning of the dark period, t is time from the start of the dark reaction, and p_d is the degree of double bond conversion in the dark.*

These models allow to evaluate the following parameters: k_t^m and $k_p[P^*]_0$ (model I); $k_t^b[P^*]_0$ and $k_p[P^*]_0$ (model II); and k_t^m, $k_t^b[P^*]_0$ and $k_p[P^*]_0$ (model III).

Model II, which assumes bimolecular termination only, in its simplified partly integrated form, has been widely used for the determination of propagation and termination rate coefficients at various degrees of conversion of double bonds [5]. For calculations, the experimental data are usually taken over the period of the first several to a few tens of seconds of the reaction proceeding in the dark. Thus, the values of the calculated rate coefficients are averaged over this period of time of the dark reaction. They are assumed to be representative of the rate coefficients during the polymerization under continuous illumination at a given conversion degree.

However, the rate coefficients obviously vary with the time of the reaction occurring in the dark. Moreover, the termination mechanism also changes. Under illumination, at the early and medium polymerization stages, mobile short-chain radicals able to diffuse are formed and the bimolecular termination is dominated by the reactions involving these radicals with macroradicals connected to the network. However, in the dark, the formation of short-chain radicals is abruptly stopped which immediately affects the bimolecular process. The entire living population is growing longer (including the short-chains not terminated before) and mobilities of macroradicals are dropping rapidly [7]; so, we may expect also a rapid drop in the bimolecular termination rate coefficient k_t^b. In turn, the monomolecular termination rate coefficient, k_t^m, which represents a fraction of radicals immobilized in the polymer network (eliminated from further reactions) per second, should increase as the time of dark reaction is protracted.

In this work we tried to model such a process. Using three termination models, we characterized the changes in the rate coefficient and the termination mechanism governing in the time of the dark reaction.

EXPERIMENTS AND CALCULATIONS

(Diethylene glycol) dimethacrylate (Aldrich) was selected as the model monomer. Experimental conditions were the same as described elsewhere [5]. Reaction rate profiles and conversions were determined by differential scanning photocalorimetry. Polymerization was initiated with a 366-nm light supplied from a medium pressure Hg lamp (incident light intensity, 1.3 mW/cm^2) in the presence of 2,2-dimethoxy-2-phenylacetophenone used at a concentration of 0.03 M. Irradiation was carried out at 40°C in an argon atmosphere.

The rate coefficients for each model (eqs. (1)—(3)) were calculated by the non-linear least-squares method. To find the termination model that fits best to the experimental data, statistical analysis based on the Snedecor's test was used at a confidence level $\alpha = 0.05$. Details of the calculations have been given elsewhere [4, 5].

RESULTS AND DISCUSSION

Initiation was stopped at five various degrees of double bond conversion (0.03, 0.11, 0.24, 0.39 and 0.60, Fig. 1). These conversions were denoted as starting conversions.
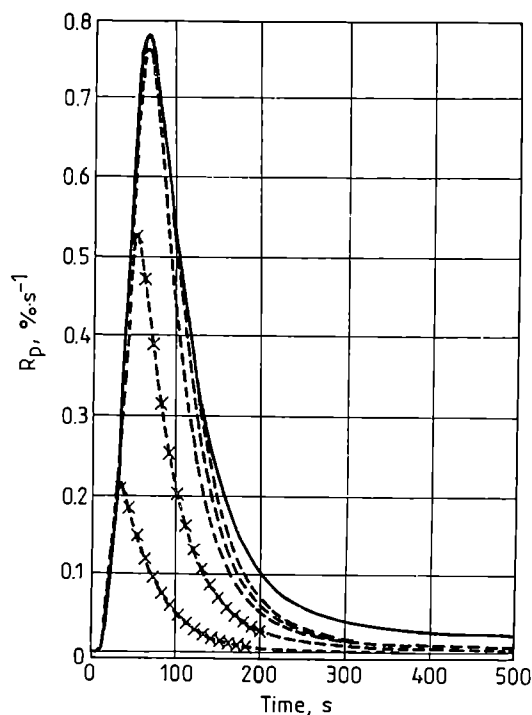

Fig. 1. Rate of polymerization vs. time for five dark reactions occurring after irradiation was stopped at 0.03, 0.11, 0.24, 0.39 and 0.60 double bond conversion (starting conversion); points on curves show time intervals (10 s) used for modeling; the uppermost curve shows the polymerization occurring under continuous exposure

To find the dependence of k_t''', $k_p[P^\bullet]_0$, and $k_t^b[P^\bullet]_0$ on the time of the dark reaction, the postpolymerization curves were divided into segments corresponding to time intervals of 10 s. The rate coefficients were calculated at various times of postpolymerization (10, 20, 30 s, etc., up to 160 s), always starting from the point of discontinuation of irradiation. Thus, the propagation and termination rate coefficients were averaged over larger and larger dark conversions. In this way, $[P^\bullet]_0$ is always constant for a given dark reaction. Such a procedure enables the kinetic parameters calculated for increasingly long times of dark reaction within one starting conversion to be intercompared.

The statistical analysis indicated that, at the beginning of postpolymerization, the experimental data were best described by model II. This fact means that the termination process occurred mainly via a bimolecular reaction involving macroradicals. However, at longer times of the dark reaction, the statistical analysis showed the mixed termination model (model III) to yield the best fit to the experimental data, indicating the occurrence and the increasing importance of monomolecular termination (radical trapping).

Figures 2—4 present the results of calculations expressed as dependence of rate coefficients on total (during illumination and in the dark) degree of double bond conversion. The results are plotted in series. Each point corresponds to one time interval of the dark reaction (and a conversion increment during the dark reaction). In Figs. 2 and 3, the first point in each series corre-

sponds to the starting conversion at which the initiation has been discontinued and shows the results for the first 10 s of the dark reaction. The other points correspond to the conversions of double bonds during 20, 30, etc. seconds of the dark reaction and to the rate coefficients calculated for this reaction time (corresponding conversion increment).

Figure 2 shows the results obtained by the use of model II. Arrows indicate the change in the termination mechanism from the bimolecular to the mixed one. So, for this model, only points corresponding to the time intervals where bimolecular termination dominates should be considered. It is worthy to stress that the bimolecular mechanism is not exclusive, but dominating only. The results obtained indicate that k_p (average value for monomeric and pendant double bonds) remains practically constant during the after-effect. On the other hand, k_t^b rapidly increases although it is expected to decrease. However, any decrease in the termination rate coefficient together with the constant propagation rate coefficient should lead to an increase in the polymerization rate. Because in the dark the polymerization rate rapidly decreases, model II, which assumes only one mechanism of termination, compensates it by an increase in $k_t^b[P^\bullet]_0$. Taking into account that, in model II, k_t^b represents all the types of processes leading to termination, the time behavior of the calculated k_t^b may be suspected to be modified by the strong growing tendency of k_t'''. The bimolecular termination model is thus seen to fail to render the postpolymerization process well.

Because during the shortest times of the dark reaction the bimolecular termination dominated, statistical analy-
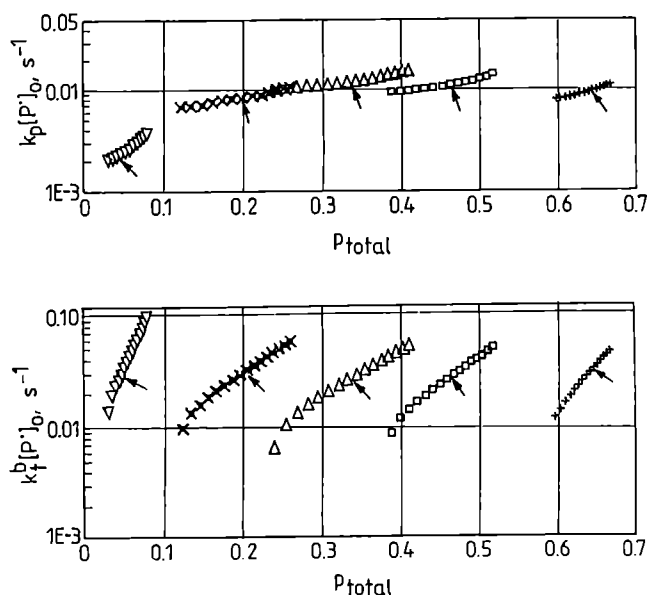

Fig. 2. Model II rate coefficients in relation to the total degree of double bond conversion. The results in series correspond to starting conversions 0.03 (▽), 0.11 (×), 0.24 (△), 0.39 (□) and 0.60 (+) and are given for all time intervals, regardless of the model indicated by statistical analysis to yield the best fit to the corresponding segment of the curve. Arrows indicate changes in termination mechanism from the bimolecular to the mixed one
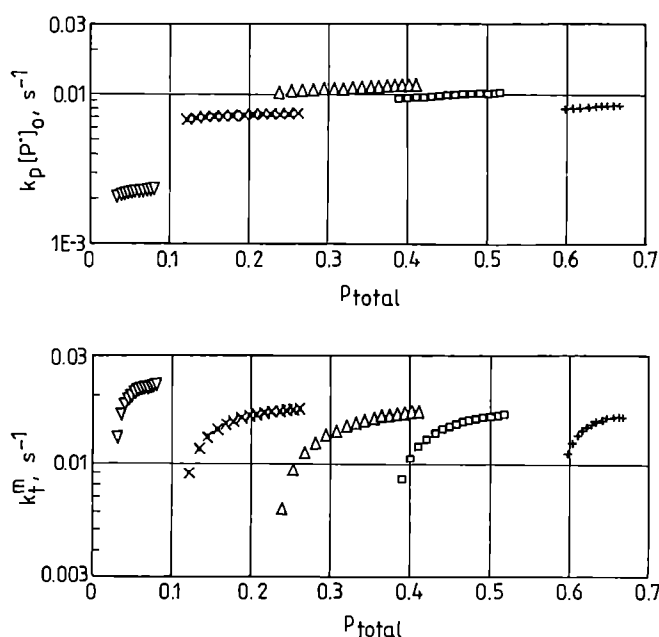

Fig. 3. Model I rate coefficients in relation to the total degree of double bond conversion. For symbols, see Fig. 2. The results are given for all time intervals, regardless of the model indicated by statistical analysis to yield the best fit to the corresponding segment of the curve
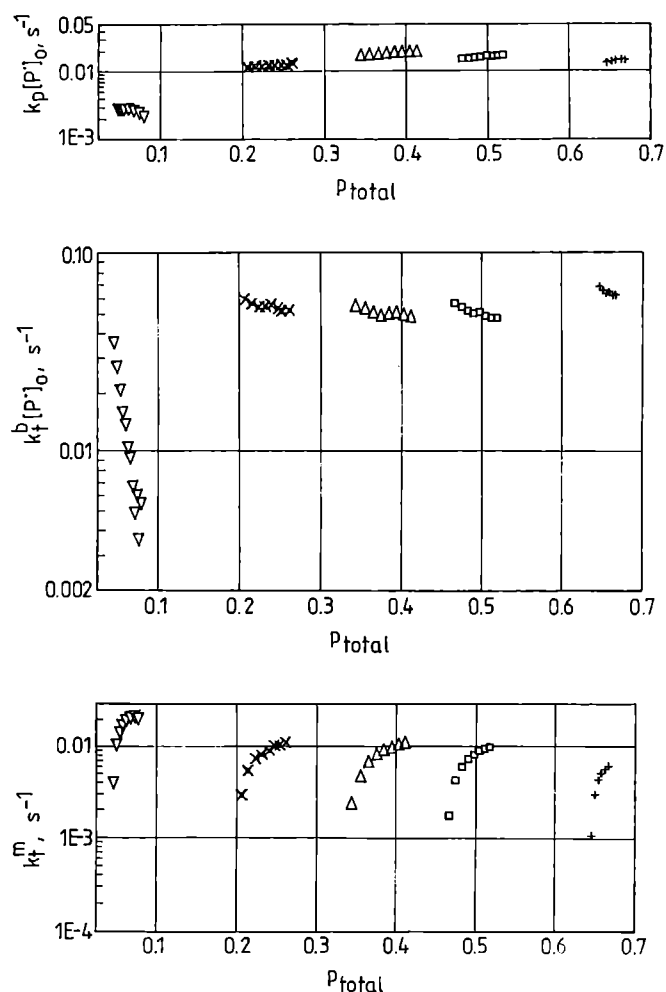
Fig. 4. Model III rate coefficients in relation to the total degree of double bond conversion. For symbols, see Fig. 2. The parameters are given only for the time intervals where results were best reproduced by the model

sis could never indicate the monomolecular reaction to be the main termination way. Despite it, we present also the results obtained by the use of model I (Fig. 3). The k_t'''-value which now represents all the termination processes, increases as the conversion in the dark is increased. To explain this result in terms of the assumptions underlying model I, we may say that an increasingly great number of radicals in the time unit become immo-

bilized in the network and excluded from further reaction (under the time scale measured by photocalorimetry).

The results obtained by the use of the mixed termination model (III) are shown in Fig. 4. In this case, the parameters for measurements best reproduced by the model are given only. Again, practically constant levels of k_p are observed. However, in contrast to model II, $k_t^b[P^\bullet]_0$ values decrease as the dark reaction proceeds. This fact means that the collision of two radicals linked to the polymer network (the only radicals existing far in the dark) becomes more and more difficult. The drop of k_t^b is moderated at medium conversions by the reaction diffusion mechanism [6]. At the same time, radicals are continuously eliminated from propagation due to the monomolecular termination (growing k_t''').

Concluding we can say that only the mixed termination model seems to reproduce well the time behavior of the rate coefficients during the dark reaction, *i.e.*, an increase in k_t''' values and a decrease in $k_t^b[P^\bullet]_0$ values.

REFERENCES

1. Kurdikar D. L., Peppas N. A.: *Macromolecules* 1994, **27**, 4084.
2. Timpe H.-J., Strehmel B.: *Macromol. Chem.* 1991, **192**, 771.
3. Müller U., Jockusch S., Timpe H.-J.: *J. Polym. Sci., A: Polym. Chem.* 1992, **30**, 2755.
4. Andrzejewska E., Bogacki M. B.: *Macromol. Chem. Phys.* 1997, **198**, 1649.
5. Andrzejewska E., Bogacki M. B., Andrzejewski M., Tymińska B.: *Polimery* 2000, **45**, 502.
6. *cf.* review articles: Anseth K. S., Newman S. M., Bowman C. N.: *Adv. Polym. Sci.* 1995, **122**, 177; Andrzejewska E.: *Prog. Polym. Sci.* 2001, **26**, 605.
7. O'Shaughnessy B., Yu J.: *Macromolecules* 1998, **31**, 524.

LUDZIE NAUKI

Jubileusz 70-lecia
PROFESORA LUDOMIRA ŚLUSARSKIEGO

Profesor Ludomir Ślusarski urodził się w 1931 r. w Konstantynowie. W roku 1955 uzyskał dyplom magisterski na Wydziale Chemicznym Politechniki Łódzkiej i tam też rozpoczął karierę naukową oraz dydaktyczną. Jeszcze podczas studiów w 1954 r. został zatrudniony na stanowisku asystenta w katedrze Technologii Kauczuków i Gumy PŁ. Z macierzystą Uczelnią pozostaje związany do chwili obecnej. W 1963 r. uzyskał stopień doktora, w roku 1987 doktora habilitowanego, a w 1990 r. tytuł profesora. W roku 1995 został powołany na stanowisko profesora zwyczajnego Politechniki Łódzkiej. Od 1972 r. jest kierownikiem Zakładu Technologii Kauczuków i Gumy przekształconego następnie w Zakład Technologii Polimerów, a od roku 1989 — dyrektorem Instytutu Polimerów. W latach 1996—99 był członkiem Senatu Politechnik Łódzkiej i przewodniczącym Senackiej Komisji ds. Budżetu i Finansów; ponadto w latach 1997—2000 — członkiem Komitetu Badań Naukowych. Od wielu lat wykłada kilka przedmiotów związanych z podstawami chemii i technologii oraz inżynierii materiałowej polimerów. W zakresie tej specjalności wypromował 280 magistrów inżynierów oraz 8 doktorów. Z Jego inicjatywy uruchomiono w Politechnice Łódzkiej kierunek nauczania „Inżynieria materiałowa polimerów".

Profesor Ślusarski jest autorem lub współautorem blisko 200 artykułów naukowych, w tym kilku rozdziałów w podręcznikach i monografiach wydanych w kraju (2) i za granicą (4), oraz ponad 20 patentów stanowiących podstawę kilkunastu technologii wdrożonych w przemyśle. Jest twórcą szkoły naukowej w dziedzinie technologii i inżynierii materiałowej elastomerów. Wielokrotnie był zapraszany do udziału w komitetach naukowych konferencji krajowych i zagranicznych, jak również do wygłaszania referatów plenarnych bądź sekcyjnych. Profesor był także organizatorem lub współorganizatorem kilkunastu międzynarodowych konferencji naukowych. Utrzymuje kontakty z zagranicznymi ośrodkami naukowymi — uniwersytetami Claude Bernard w Lyonie, Górnej Alzacji w Miluzie, Strathclyde w Glasgow oraz Deutsches Institut für Kautschuktechnologie. Współpracuje w szerokim zakresie z przemysłem, Polską Akademią Nauk i licznymi organizacjami naukowymi.

Profesor Ślusarski przewodniczy radom naukowym w Instytucie Przemysłu Gumowego „Stomil" i Instytucie Inżynierii Materiałów Włókienniczych oraz jest członkiem Rady Naukowej Instytutu Włókien Chemicznych. Ludomir Ślusarski należy do grona założycieli Polskiego Towarzystwa Kalorymetrii i Analizy Termicznej, jest też członkiem Komitetu Nauki o Materiałach PAN i przewodniczącym Sekcji „Materiały Polimerowe", członkiem Komitetu Chemii Analitycznej PAN i przewodniczącym Komisji Analizy Polimerów, wiceprzewodniczącym Rady Naukowej Centrum Chemii Polimerów w Zabrzu, członkiem Rady Naukowej Centrum Badań Molekularnych PAN w Łodzi, członkiem Akademii Inżynierskiej. Jest przewodniczącym Rady redakcyjnej w czasopismach „Elastomery" i „Rubber Review", członkiem Rad programowych czasopism „Polimery", „Archiwum Nauki o Materiałach", „Kompozyty" i „Plastic Review". Będąc także członkiem European Access Network (EAN) pełni jednocześnie funkcje przedstawiciela Polski w Executive Committee EAN. Należy do

Prof. L. Ślusarski w rozmowie z dr. S. Wolffem na konferencji w Norymberdze, lipiec 1997 r.
Prof. L. Ślusarski conversing with Dr. S. Wolff at the Conference in Nürnberg (July 1997)

Polskiego Towarzystwa Chemicznego, Polskiego Towarzystwa Materiałów Kompozytowych i American Chemical Society.

Długa jest lista odznaczeń, które Profesor otrzymał za działalność naukową, mianowicie: Krzyż Kawalerski Oficerski OOP, Złoty Krzyż Zasługi, Medal Edukacji Narodowej, odznaki „Zasłużony dla Politechniki Łódzkiej", srebrna „Zasłużony dla Górnictwa", honorowa SITPChem i srebrna honorowa NOT.

Prof. L. Ślusarski jest bardzo zaangażowany w sprawy Uczelni i Instytutu. Zawsze dbał i dba nadal o rozwój młodej kadry naukowej. Współpracownicy mogą liczyć na jego pomoc oraz życzliwe rady — inspiruje i zachęca do podejmowania ambitnych zadań naukowych. Utrzymuje bliskie, przyjacielskie kontakty z wieloma naukowcami zagranicą.

Marian Zaborski
Politechnika Łódzka
Instytut Polimerów

KALENDARZ IMPREZ

16—20 czerwca 2002 r. Guimarães, Portugalia. „**Eighteenth Annual Meeting — PPS-18 Polymer Processing Society"**.

Organizatorzy: Polymer Processing Society, Akron, Ohio, USA + University of Minho, Guimarnes, Department of Polymer Engineering.

Tematyka: mieszanie, sporządzanie mieszanek gumowych i mieszanin polimerowych; przetwarzanie reaktywne, formowanie wytłoczone, formowanie wtryskowe i formy, formowanie wirowe, reologia i reometria, modelowanie procesów, prace rozwojowe związane ze strukturą, właściwości i testy eksploatacyjne, kompozyty, nowatorskie procesy i zastosowania, monitorowanie procesu i regulacja, czujniki pomiarowe.

Zgłaszanie materiałów referatowych i posterowych (1-stronicowych) do 15 października 2001 r.

Informacje: PPS-18 Organizing Secreatariat, Department of Polymer Engineering, Campus Azurém, 4800-058 Guimarnes, Portugal. Tel.: +351 253 510 245, fax: +351 253 510 249, e-mail: pps18.dep.uminho.pt; http://www.dep.uminho.pt/pps-18.

8—11 września 2002 r. Ostenda, Belgia. 2. Międzynarodowe sympozjum nt. materiałów wyjściowych i nowatorskich technik recyklingu tworzyw sztucznych: „**Feedstock Recycling of Plastics and Other Innovative Plastics Recycling Techniques — ISFR'2002"**.

Organizatorzy: Research Association for Feedstock Recycling of Plastics, Japan (FSRJ); Plastic Waste Management Institute, Japan (PWMI); Association of Plastics Manifacturers Europe, Belgium (APME); European Council of Vinyl Manufacturers, Belgium (ECVM).

Tematyka: Recykling odpadów z zastosowaniem pirolizy i solwolizy, produkcja gazu syntezowego drogą gazyfikacji lub pirolizy oksydacyjnej, uzysk energii z przetwarzania odpadów tworzyw sztucznych, gumy i innych wysokokalorycznych źródeł ciepła; techniki innowacyjne recyklingu mechanicznego włączające naukowe i badawcze czynniki logistyczne i ekonomiczne w zbiórce, sortowaniu, przetwarzaniu i dokumentacji produktu oraz poszerzaniu rynków zbytu.

Informacje: Mrs. Kristel Praet, M.Sc., Research and

Development Belgium (RDB), Leo de Bethunelaan 80, 9300 Aalst, Belgium. Tel/fax: 00 32 53 78 63 55, e-mail: kristel.praet@skynet.be + Prof. Dr. Ir. A. Buekens, Free University of Brussels, Dept. Chemical Engineering CHIS-2, Pleinlaan 2, 1050 Brussels, Belgium. Tel.: 00 32 2 629 3247, e-mail: abuekens@vub.ac.be.

30 września—4 października 2002 r. Birmingham, W. Brytania. „**Interplas 2002"** — Europejska wystawa tworzyw sztucznych i gumy.

Organizatorzy: Reed Exhibition Companies (REC) + UK's Polymer Machinery Manufacturers + Distributors Association (PMMDA).

Informacje: Syreeta Tranfield, Reed Exhibition Companies, tel.: 44(0) 181 910 7947, 44(0) 208 010 7947, fax: 44(0) 181 190 7829, e-mail: syreeta.transfield@reedexpo.co.uk.

4—8 listopada 2002 r. Taipei, Tajwan. „**Polymer Processing Society — Asia/Australia Meeting PPS-2002"**.

Organizatorzy: Chang Gung University + The Polymer Processing Society, Taipei.

Tematyka ogólna: formowanie wtryskowe, wytłaczanie, reologia mieszaniny i stopy polimerowe, prace związane z rozwojem zagadnień morfologii i struktury polimerów, kształtowanie termiczne, formowanie z rozdmuchiwaniem, formowanie obrotowe, modelowanie matematyczne, przetwarzanie reaktywne, kompozyty polimerowe, włókna i folie, sporządzanie mieszanek gumowych i mieszanin polimerowych, właściwości mechaniczne, optyczne i elektryczne.

Tematyka specjalistyczna: przetwarzanie żywności, uwidocznianie przepływu, czujniki w procesie przetwarzania, formowanie wtryskowe wspomagane gazem, biopolimery, zastosowania w optyce i elektronice/elektrotechnice, nowe procesy przetwórcze.

Informacje: Dr Shih-Jung Liu, PPS Meeting 2002, Polymer Rheology and Processing Lab, Mechanical Eng., tel.: 886-3-3288 566, fax: 886-3-3972 558, e-mail: shihjung@mail.cgu.edu.tw lub pps2002@mail.cgu.edu.tw; http://pps.cgu.edu.tw.