

Chain Extension of Poly(ethylene terephthalate) with Bisphenol-A Dicyanate

Yanjun Zhang,¹ Chen Zhang,¹ Hangquan Li,¹ Zhongjie Du,¹ Congju Li²

¹The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

²Beijing Key Laboratory of Clothing Material R and D and Assessment, Beijing Institute of Fashion Technology, Beijing 100029, People's Republic of China

Received 31 May 2009; accepted 21 January 2010

DOI 10.1002/app.32136

Published online 5 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Chain extension of poly(ethylene terephthalate) (PET) with bisphenol-A dicyanate (BADCy) was studied using an internal mixer under reactive blending conditions. The reaction between PET and BADCy was confirmed by Fourier transform infrared (FTIR) and chemical titration. With increasing amount of BADCy introduced, the modified PET gave rise to higher torque during stirred in an internal mixer, higher viscosity (η'), and

higher storage modulus (G'). Measurement of intrinsic viscosity showed that BADCy indeed extended the molecular weight of PET. DSC analysis represented that T_m and T_c of the modified PET were shifted to low temperatures. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2003–2008, 2010

Key words: poly(ethylene terephthalate) (PET); bisphenol-A dicyanate (BADCy); chain extension

INTRODUCTION

Poly(ethylene terephthalate) (PET) has been widely used in packaging fields due to its transparency, chemical resistance, and barrier properties.¹ However, during melt processing the molecular weight of PET may be easily reduced when subjected to thermal oxidation and hydrolytic degradation.² The thermal cleavage of the PET ester bond results in carboxyl and vinyl ester end groups,³ as shown in Scheme 1. Also at processing temperature, hydrolysis reactions occur between water and PET, resulting in shorter chains with carboxylic acid and hydroxyl ester end groups (Scheme 2).⁴ Both degradations lead to reduction in molecular weight and an overall decrease in melt viscosity and melt strength,⁵ which limited its processings such as blow-molding and extrusion foaming.⁶

To balance the degradation of PET during melt processing, reactive extrusion was commonly practiced, in which di- or polyfunctional compounds were introduced to react with end groups of PET resulting chain extending and/or branching.⁷ Ring-opening type extenders were also employed because

of their high reaction rate and free of by-products. Several modifiers were proposed, including bis(epoxides) or diepoxides,^{8,9} dianhydrides,^{10–12} bisoxazolines,¹³ diisocyanates,¹⁴ triphenyl phosphate,¹⁵ and trimethyl trimellitate.¹⁶

In the research work of this group, bisphenol-A dicyanate (BADCy) was tried as an extender of PET and compared with conventional ones like diglycidyl ether of bisphenol-A (DGEBA) and methylenediphenyl diisocyanate (MDI). When the content of extender was 1 phr, the torque maximum of DGEBA, MDI, and BADCy were 1.1, 2.5, and 3.9 Nm, respectively. It was found that BADCy being more effective and worthy further studying. In this paper, the investigation of BADCy as an extender was reported. The chain extending reaction was carried out in an internal mixer using various processing parameters like rotor speed and feed composition. The extending effect was characterized with torque, intrinsic viscosity, and the carboxyl content.

EXPERIMENTAL

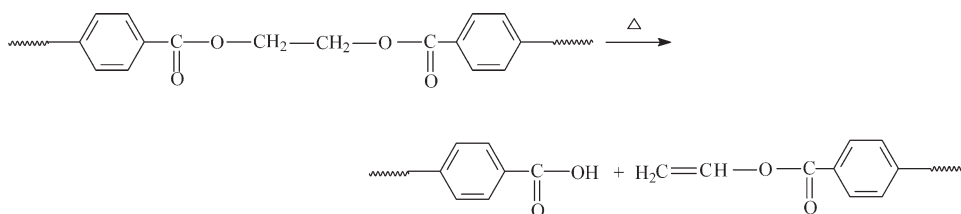
Materials

An industrial grade PET of intrinsic viscosity $[\eta]$ 0.68 dL/g was supplied by Yanshan Petrochemical Co., China. Before processing, PET was dried at 140°C in vacuum for 6 h. Bisphenol-A dicyanate (BADCy) was supplied by Huifeng Technical & Business Co., China. The molecular structure of BADCy was shown in Scheme 3. Phenol was

Correspondence to: Z. Du (duzj@mail.buct.edu.cn) or C. Li (congju@sina.com).

Contract grant sponsor: The 863 Project; contract grant number: 2007AA021900.

Contract grant sponsor: PHR(IHLB).



Scheme 1 Thermal degradation reaction during melt processing of PET.

supplied by Fuchen Chemical Reagents Factory, China. 1,1,2,2-tetrachloroethane and chloroform were supplied by Sinopharm Chemical Reagent Beijing Co., China. Benzyl alcohol and phenol red were supplied by Beijing Yili Fine Chemicals Co., China.

Chain extension reaction

Chain extension reaction was carried out in an internal mixer (Haake, Rheomix 600). Preweighed dry PET was loaded to the mixer chamber and subjected to stirring at 60 rpm and 230°C. After the PET granules became melted, BADCy was added at 1–3 phr. The reactive mixing continued for an additional period of about 10 min with temperature and torque continuously registered. No specific precaution was taken to preserve the melt from the oxygen atmosphere during the experiments.

Characterization

Fourier transform infrared (FTIR) spectrometer (Nexus 670) was used to detect the functional groups at room temperature from powder-pressed pellet samples with KBr.

The intrinsic viscosity was measured with an Ubbelohde viscometer at 25°C. The diluted solution for determination was prepared by dissolving 125 mg of the sample in 25 mL of a mixed solvent of phenol/tetrachloroethane (60/40 w/w).

The carboxyl content was determined according to Pohl's method¹⁷ by titrating a standard NaOH solution into a solution of PET in benzyl alcohol/chloroform using phenol red as an indicator.

The dynamic viscosity (η') and storage modulus (G') of the extending products were measured with an oscillatory rheometry (AR-2000, TA) with a 10% strain at 260°C under dry nitrogen. Parallel plates,

25 mm in diameter and a gap of 1 mm were used for the frequency sweep.

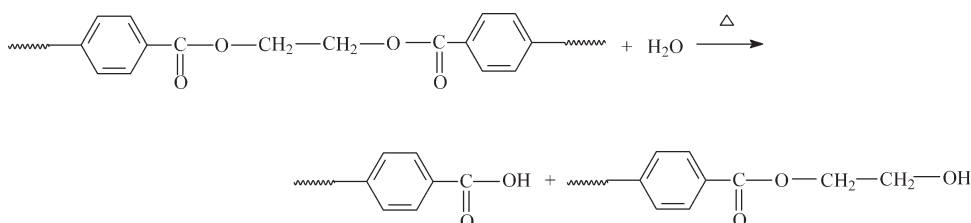
The calorimetry measurements were performed using a differential scanning calorimeter (DSC, Thermal PerkinElmer Pyris 1) under nitrogen. The samples were first heated to 300°C and held for 2 min, then cooled to 40°C at 10°C/min and heated again from 40 to 300°C at 10°C/min.

RESULTS AND DISCUSSION

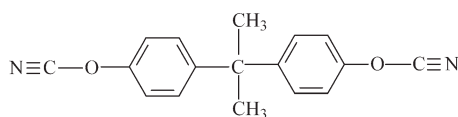
FTIR was employed to confirm the reaction between the PET and BADCy during the chain extension. The reaction was traced mainly by paying attention to the ---OCN stretching band at 2272 and 2237 cm^{-1} for the cyanate group of BADCy. As shown in Figure 1, these absorption bands of PET/BADCy samples disappeared during the chain extension process. It means BADCy indeed reacted with PET, as shown in Scheme 4.

The consumption of BADCy could also be indicated by the reduction in carboxyl content, which was determined via titration method. Table I presented the carboxyl content for various systems after mixing in an internal mixer. All the carboxyl content of the samples after reacted with 1, 2, and 3 phr of BADCy were below 20 eq/10⁶ g, which contrasted to 49.5 eq/10⁶ g for neat PET. Intuitively, reacted with a larger amount of BADCy the sample should possess lower carboxyl content. One may doubt that why the carboxyl content of the three systems were comparable. The reason was probably the chain extending was accompanied by thermal and mechanical degradation during the mixing. These degradations may yield new carboxyl groups.

As the reaction between cyanate group and carboxyl proceeded, the molecular chains of PET



Scheme 2 Hydrolysis degradation reaction during melt processing of PET.



Scheme 3 Chemical structure of BADCy.

became extended and the viscosity of the blend increased, which was demonstrated by the change in torque values, as shown in Figure 2. For a blend default of BADCy, the torque showed no increase but decreased gradually owing to the thermal-mechanical degradation. When BADCy was present, noticeable increases in torques were observed. For the traces 1, 2, and 3 phr, the more the amount of BADCy introduced, the higher and the earlier the torque maximum exhibited. The torque maxima of 3.9, 13.5, and 17.5 N m occurred at 14, 13, and 11.5 min for 1, 2, and 3 phr BADCy, respectively. The evolution of the torque maxima indeed indicated of chain extending. After the maximum, the torque became decreased and leveled off a certain value higher than initial one. This decrease was because the system became more uniform, and the end torque value indeed represented the degree of chain extending.

Interestingly, the system temperature gave rise to a similar behavior like the torque value: a maximum was showed up for each run involving chain extending, as shown in Figure 3. Like the torque values, the more the amount of BADCy introduced, the higher and the earlier the temperature maximum was given. The increase in temperature was contributed by two origins: the shear exerted by the rotor to the melt of increasing molecular weight, and the heat released from the reaction between cyanate and carboxyl groups. As a result, the larger population of the reactive groups, the more the heat released, and thus the earlier the temperature maximum was given. However, the degradation was more favored at higher temperatures, resulting in decrease in melt viscosity and thus the torque. This in turn caused the decrease in melt temperature. Consequently the reduction in temperature after the maximum was similar to that of torque.

Similar effects were observed when different stirring rate was applied in the rheomixer, shown in Figures 4 and 5. Because of the initial heterogeneity

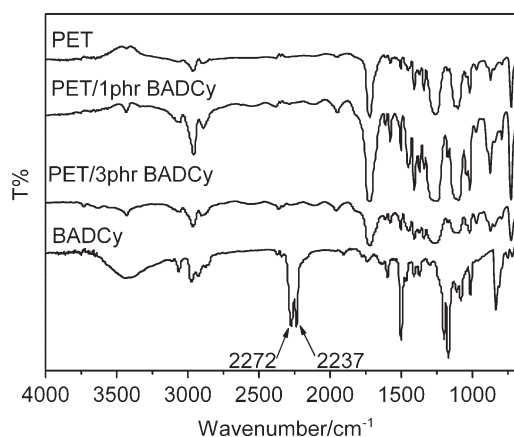
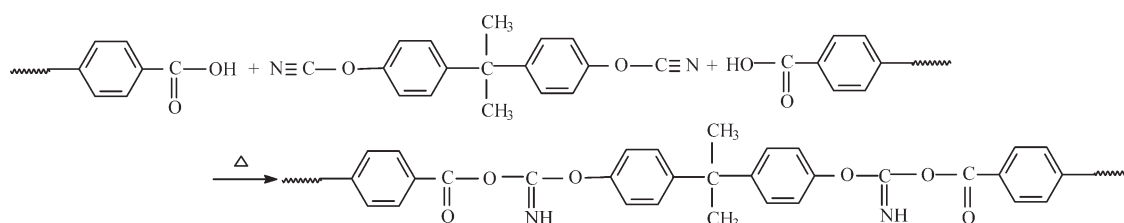


Figure 1 FTIR spectra of PET, BADCy, and PET/ BADCy samples.

of the system, a torque maximum was exhibited in each run, and naturally, the higher the stirring rate, the earlier the maximum. As a same recipe was employed, the heights of the maxima were comparable. However, the equilibrium torque after the maximum was depended on the stirring rate, the higher the stirring rate, the lower the equilibrium torque (Fig. 4). This, again, was explained by the degradation in different temperatures. As shown in Figure 5, both height and position of the maximum in temperature were stirring rate dependent. The higher the stirring rate, the higher the system temperature. The enhanced stirring rate enhanced the higher probability of accessibility of the reactive end groups and a higher rate of the chain extension reactions, which led to higher temperatures. However, the high temperature accelerated the chain cleavage. As a balanced result, the final molecular weight from higher stirring rate was lower, which was reflected by the low value of equilibrium torque.

What implied by the changes in torque and temperature was confirmed by the measurement of intrinsic viscosity $[\eta]$, which was used in this work as a measure of the molecular weight. As shown in Table II, by the end of mixing, i.e. 10 min after the addition of BADCy, intrinsic viscosities of 0.87, 0.81, and 0.79 dL/g were retained for stirring rates of 40, 60, and 80 rpm, respectively. As explained above, it was the higher temperature caused by higher-rate stirring that resulted in more severe degradation.



Scheme 4 Reaction between PET end groups and BADCy.

TABLE I
Carboxyl Content (CC) of PET/ BADCy System at Different Stages of Mixing
(Stirring Rates = 60 rpm)

BADCy content (phr)	CC (eq/10 ⁶ g)				
	8 min	11 min	14 min	17 min	18 min
0	26.3	33.1	37.7	39.6	49.5
1	25.5	7.8	11.3	11.3	16.5
2	26.3	9.4	7.6	15.5	18.1
3	24.2	13.9	15.2	14.4	18.4

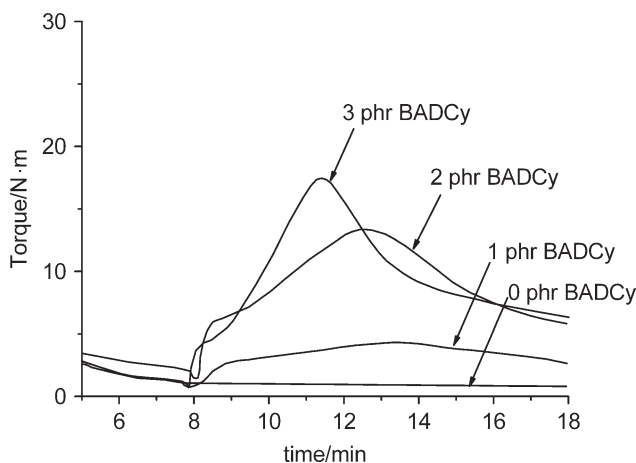


Figure 2 The effect of BADCy content on the torque of PET processed at 230°C and 60 rpm.

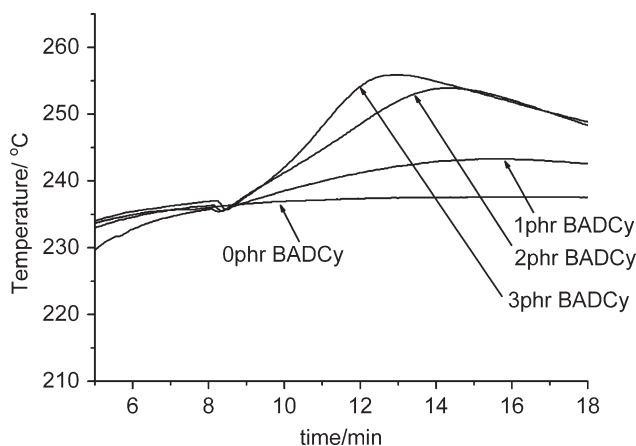


Figure 3 The effect of BADCy content on the melt temperature of PET processed at 230°C and 60 rpm.

Figure 6 presented the $[\eta]$ values measured at different stages of mixing with various BADCy loadings. As seen, a higher loading of BADCy did not result in higher molecular weight, because of the negative effect of reaction heat. Besides, obvious increase in molecular weights could be achieved at the middle of reaction, however, only a fraction of the increase was reserved at the end of the mixing. Nevertheless, even by the highest stirring rate, 80 rpm, which was

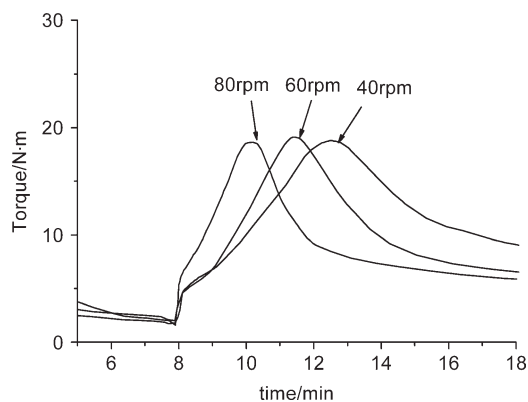


Figure 4 The effect of stirring rate on the torque of PET processed at 230°C (BADCy content = 3 phr).

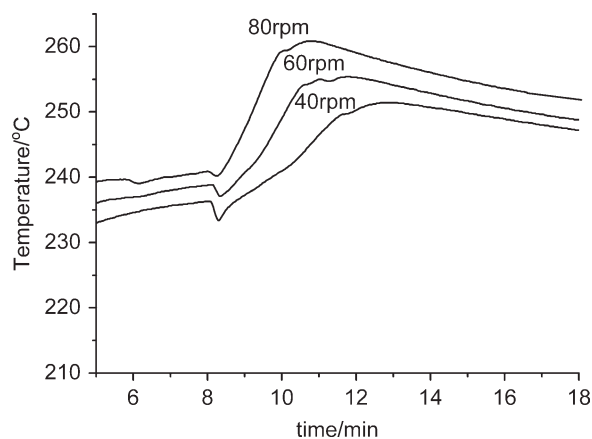


Figure 5 The effect of stirring rate on the melt temperature of PET processed at 230°C (BADCy content = 3 phr).

much more severe than that in the practical processing condition, the ending intrinsic viscosity was considerably higher than the plain sample, this indicated that the chain extending was still effective.

The chain extension through reaction with BADCy could be further confirmed by the melt viscosity (η') in Figure 7 and melt modulus (G') in Figure 8, both measured with an oscillatory rheometry. It was seen that at the entire frequency range of 0.1 to 100 rad/s, the viscosity of extended PET was one order of magnitude higher, and the modulus was also considerably higher, than those of the neat one. As the

TABLE II
Intrinsic Viscosity and Carboxyl Content (CC) of PET/
BADCy System After 10 min of BADCy Addition at
Different Stirring Rates (BADCy Content = 3 phr)

Stirring rate (rpm)	$[\eta]$ (dL/g)	CC (eq/10 ⁶ g)
40	0.87	16.8
60	0.81	18.4
80	0.79	18.3

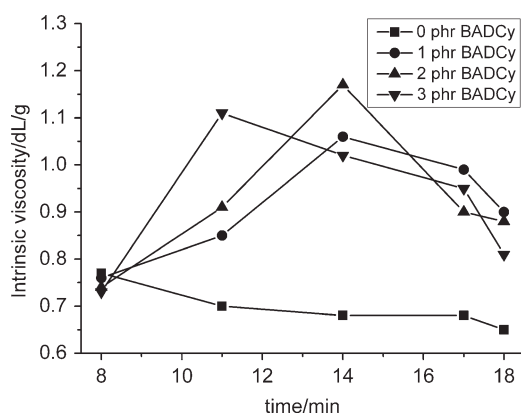


Figure 6 Intrinsic viscosity of PET/ BADCy system at different stages of mixing (Stirring rate = 60 rpm).

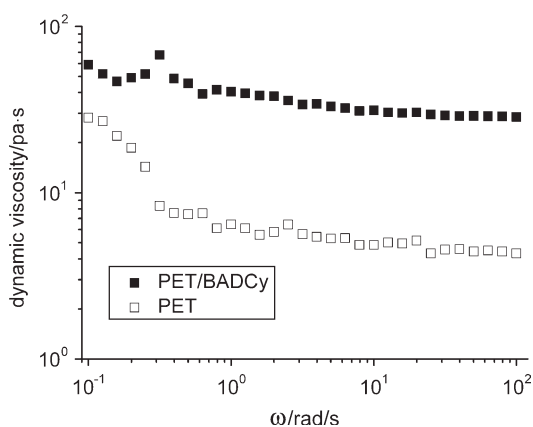


Figure 7 Dynamic viscosity versus frequency for PET and PET/BADCy (BADCy content = 1 phr).

viscosity and modulus data were similar for systems based on 1, 2, and 3 phr BADCy, only those for 1 phr were shown for clarity.

The DSC cooling and heating thermograms of neat and extended PETs were presented in Figure 9 and the data were summarized in Table III. As seen in Figure 9(A) and Table III, upon reacted with

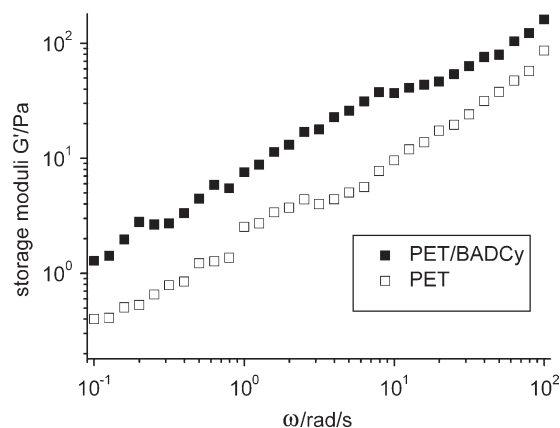


Figure 8 Storage modulus versus frequency for PET and PET/BADCy (BADCy content = 1 phr).

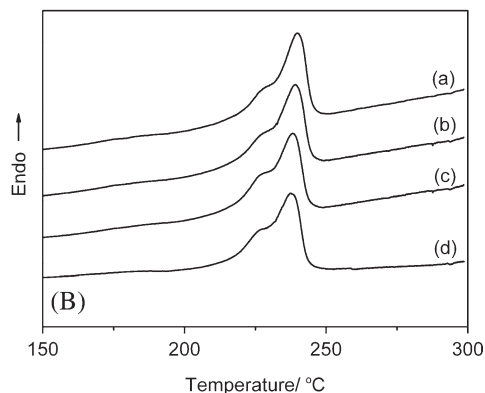
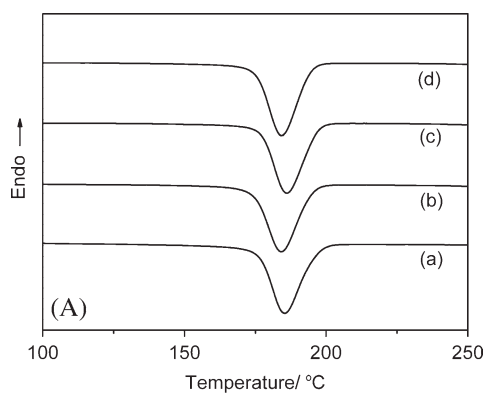


Figure 9 DSC cooling scans (A) and heating scans (B) of PET and PET/BADCy at the rate of 10°C/min (a) PET (b) PET/1 phr BADCy (c) PET/2 phr BADCy (d) PET/3 phr BADCy.

BADCy, crystallization temperature (T_c) and heat of melt crystallization (ΔH_c) shifted to lower values than those of the neat one because of reduced mobility of extended PET chains and thus the difficulty in crystallization. The melting information was provided by the heating scans in Figure 9(B). The neat PET gave rise to melting peak placed at 240°C, while

TABLE III
DSC Data of PET and PET/BADCy

Sample	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PET	240	36.4	185	41.9
PET/1phr BADCy	239	37.3	184	40.6
PET/2phr BADCy	238	39.0	186	41.5
PET/3phr BADCy	237	43.0	184	41.2

those for PET/BADCy samples at 239, 238, and 237°C. The lower melting temperatures suggested the less perfect crystallization of the extended chains.

CONCLUSIONS

PET was chain extended by reacted with BADCy in the molten phase. The melt viscosity and elasticity of the extended PET were considerably higher than those of plain one. When the PET/BADCy system was stirred in an internal mixer, torque and temperature maxima were observed, which may be considered as indicators of the reaction between PET and BADCy. The higher the loading of BADCy, or the greater the stirring rate, the earlier the torque maximum and the higher the temperature maximum. The reduced mobility of the extended PET resulted in less perfect crystal, which was witnessed by the difficulty in crystallization, the lower melting temperatures.

References

- Lagaron, J. M.; Catala, R.; Gavara, R. *Mater Sci Technol* 2004, 20, 1.
- Pohl, H. A. *J Am Chem Soc* 1951, 73, 5660.
- Samperi, F.; Puglisi, C.; Alicata, R.; Montaudo, G. *Polym Degrad Stab* 2004, 83, 3.
- Campanelli, J. R.; Kamal, M. R.; Cooper, D. G. *J Appl Polym Sci* 1993, 48, 443.
- Dhavalikar, R.; Yamaguchi, M.; Xanthos, M. *J Polym Sci Part A: Polym Chem* 2003, 41, 958.
- Xanthos, M.; Wan, C.; Dhavalikar, R.; Karayannidis, G. P.; Bikiaris, D. N. *Polym Int* 2004, 53, 1161.
- Bikiaris, D. N.; Karayannidis, G. P. *J Polym Sci Part A: Polym Chem* 1996, 34, 1337.
- Haralabakopoulos, A. A.; Tsiourvas, D.; Paleos, C. M. *J Appl Polym Sci* 1999, 71, 2121.
- Franceise, F.; Claire, H.; John, F.; Jean-Pierre, P. *J Appl Polym Sci* 2003, 87, 1995.
- Yilmazer, U.; Xanthos, M.; Bayram, G.; Tan, V. *J Appl Polym Sci* 2000, 75, 1371.
- Firas, A.; Fugen, D. *Polym Eng Sci* 2004, 44, 1579.
- Forsythe, J. S.; Cheah, K.; Nisbet, D. R.; Gupta, R. K.; Lau, A.; Donovan, A. R.; Oshea, M. S.; Moad, G. *J Appl Polym Sci* 2006, 100, 3646.
- Karayannidis, G. P.; Psalida, E. A. *J Appl Polym Sci* 2000, 77, 2206.
- Torres, N.; Robin, J. J.; Boutevin, B. *J Appl Polym Sci* 2001, 79, 1816.
- Cavalcanti, F. N.; Teofilo, E. T.; Rabello, M. S.; Silva, S. M. L. *Polym Eng Sci* 2007, 47, 2155.
- Bikiaris, D. N.; Karayannidis, G. P. *Polym Int* 2003, 52, 1230.
- Pohl, H. A. *Anal Chem* 1954, 26, 1614.