

# Synthesis of Poly(vinyl propionate) from Poly(vinyl alcohol) in Nonaqueous Medium Using Ethyl Nitrate Dimethyl Sulfoxide as a Catalyst

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**ABSTRACT:** Poly(vinyl alcohol) (PVA) can be dissolved in a nonaqueous medium in the presence of catalytic concentration of ethyl nitrate dimethyl sulfoxide,  $C_2H_5ONO_2 \cdot DMSO$ . From the PVA solution, poly(vinyl propionate), PVPR was prepared by the homogeneous esterification of PVA with propionic acid. The ester thus formed contained some unconverted hydroxyl group. The formation of the ester was confirmed by the IR and  $^1H$ -NMR spectra. The molecular weight of the ester was determined by GPC and intrinsic viscosity ( $\eta$ ) was determined by viscometric method. Glass transition

temperature,  $T_g$ , was obtained from differential scanning calorimetric (DSC) analysis. Thermal stabilities of the ester were checked by thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) analysis. The efficiency of the ester as a flow improver of crude oil was also examined. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5675–5679, 2006

**Key words:** ethyl nitrate dimethyl sulfoxide; poly(vinyl alcohol); poly(vinyl propionate)

## INTRODUCTION

Industrially, poly vinyl esters are prepared either by the polymerization of the vinyl esters or by the transvinylation method.<sup>1–4</sup> A survey of literature indicated that the preparation of poly(vinyl propionate)<sup>4–6</sup> is done by the polymerization of vinyl propionate. Because of the solubility problem of PVA in organic solvent, the derivatives of PVA are synthesized in aqueous medium.<sup>7–11</sup> It is not possible to synthesize an ester by homogeneous esterification of PVA with the corresponding acid in aqueous medium. To solve this problem, a catalyst  $C_2H_5ONO_2 \cdot DMSO$  (EN DMSO) is synthesized, which can help PVA to mix with the solution in an organic solvent or in a mixed solvent. From the solution, PVPR was prepared by acid catalyzed homogeneous esterification of PVA with propionic acid. The ester was characterized by IR study,  $^1H$ -NMR study, GPC, viscometry, TGA, DTG, DSC, and by other analytical methods.

From literature, it is found that some poly(vinyl esters), such as poly(vinyl stearate), poly(vinyl benzoate), poly(vinyl laurate), poly(vinyl acrylate),<sup>12</sup> etc., prepared by polymerization of vinyl esters and anionic polymerization of methacrylic monomers<sup>13,14</sup> can act as pour-point depressants for crude oils.<sup>15</sup> There-

fore, one of the aims of this article is to examine PVPR as a pour-point depressant in crude oil.

## EXPERIMENTAL

### Materials

Poly (vinyl alcohol) (PVA), white crystalline form (BDH reagent grade; viscosity average molecular weight of 14,000; 1% of residual poly vinyl acetate (PVA)) was used without further purification. Propionic acid (BDH reagent grade) was also used without further purification. Dimethyl formamide, DMF (BDH reagent grade), benzene (BDH reagent grade), dimethyl sulfoxide, DMSO (BDH reagent grade) were purified by distillation under vacuum. Acrylic acid (BDH reagent grade) was purified according to the procedure adopted by O'Neil.<sup>16</sup> Paratoluene sulfonic acid (PTSA), (BDH reagent grade) was recrystallized from benzene. Nitric acid (BDH reagent grade) and hydrogen peroxide were of analytical grade, and were used without further purification.

EN.DMSO was prepared as mentioned earlier<sup>17</sup> by interaction of acrylic acid with conc.  $HNO_3$  in DMSO. The compound was characterized by analytical and spectral data.

## METHODS

The IR of the PVPR and PVA were recorded in the region between 4000 and 600  $cm^{-1}$  with a Bruker, Vector22 FTIR using thin film of the polymers. The

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thin film was made<sup>18</sup> by dissolving the polymer in chloroform, and then the concentrated solution was directly cast on a leveled clean glass plate. The film was dried under vacuum at 70°C for a week. Thickness of the film was 0.01 cm. In case of PVA, the solvent used was distilled water. The proton NMR was recorded with a WH-270 NMR spectrometer. The spectrum was obtained on solution containing 10% (w/v) PVPR in dimethyl sulfoxide with tetramethylsilane as an internal reference. The NMR spectrum of PVA was obtained using D<sub>2</sub>O as a solvent. Molecular weight was determined by GPC method with a Water GPC-150 C using tetrahydrofuran (THF) as the solvent at 25°C. The chromatograms were recorded using 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, 500, and 100 Å columns in series. The sample was eluted with a flow rate of 1 mL/min. Sample concentration used was 0.2% w/v, and the injection volume was 50 μL. Intrinsic viscosity ( $\eta$ ) was determined at 30°C by Ubbelohde viscometer using DMF as the solvent. The percentage of the unconverted hydroxyl groups in the ester was estimated by acetylation method.<sup>19</sup>

DSC was traced by METLER TOLEDO DSC-8228 in air medium at a scanning rate of 5°C/min from -30°C to ambient temperature using HAAKE EK90/MT cooler, and then 10°C/min up to 160°C. The glass transition temperature and crystallinity were determined by Freeman and Carroll method<sup>20</sup> from the DSC endotherm. TGA and DTG were performed using PerkinElmer thermal analyzer in air at a heating rate of 10°C/min using 5 ± 1 mg samples. To determine the pour point, the crude oil was first heated to 60°C and stirred for 10 min. Appropriate quantity of additive was added with stirring. The stirring was discontinued after 30 min. The crude oil was then cooled to 35°C under a constant cooling rate, and pour point was determined according to ASTM-D97/IP-15 without reheating.<sup>21</sup>

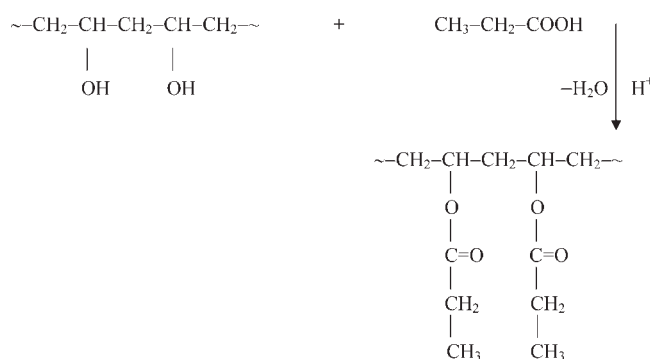
## RESULTS AND DISCUSSION

### Preparation of PVPR

PVA (4.4 g, 0.10 mol, based on -CH<sub>2</sub>-CH-OH as the repeating unit) was dissolved in 150 mL of a solvent mixture of DMF and benzene (4 : 1, v/v) in presence of EN.DMSO at 60°C in a round-bottomed flask. The molar ratio of PVA to EN.DMSO was maintained at 1 : 1.4 × 10<sup>-3</sup>. Propionic acid 8.14 g (0.11 mol) in 100 mL DMF was then added slowly to the PVA solution. Homogeneous esterification was carried out by heating the reaction mixture, at 90(± 1)°C. To get the product with different degree of esterification, the reaction time was varied from 16 to 24 h. The water produced during the reaction was removed from the reaction medium as it was formed using the Dean and Stark principle.<sup>22</sup> After completion of the reac-

tion, the solvent was removed by distilling under vacuum. The ester was precipitated by pouring into a mixed solvent of acetone and petroleum ether (1 : 2 v/v), four times in volume of the ester solution, with constant stirring. Reprecipitation was done<sup>23</sup> twice to ensure the complete removal of unreacted PVA and propionic acid. To remove PTSA, EN.DMSO, and the last traces of other impurities, the ester was washed with benzene and dried at 40°C, and stored over anhydrous calcium chloride. The yield of the product was nearly 85%.

It is proposed that the following reaction may take place between PVA and propionic acid for the production of PVPR.<sup>24</sup>



### Analysis of PVPR

Due to the formation of the ester, some interesting band appeared for PVPR. The IR spectra of PVPR and PVA are presented in Figures 1(a) and 1(b). On esterification, the O—H stretching vibration bands weakened and shifted toward higher frequencies<sup>25</sup> owing to cleavage of polymeric hydrogen bond chain. According to Hummel et al.,<sup>26</sup> infrared spectra of ali-

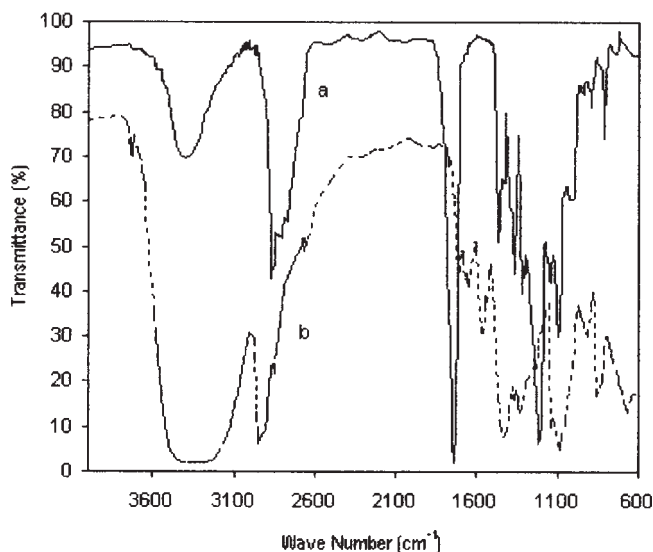


Figure 1 IR spectrum of (a) PVPR, (b) PVA (in thin film).

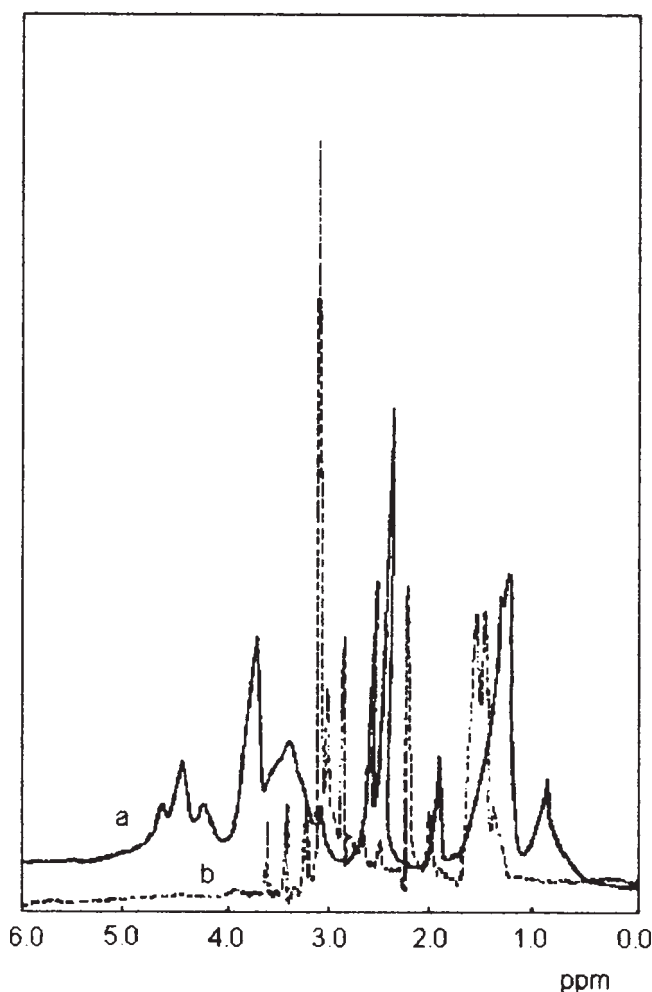


Figure 2  $^1\text{H-NMR}$  spectrum of (a) PVPR, (b) PVA.

phatic polyesters can be divided into four ranges, between  $3000$  and  $2800\text{ cm}^{-1}$ ,  $1760$  and  $1710\text{ cm}^{-1}$ ,  $1500$  and  $1100\text{ cm}^{-1}$ , and  $1100$  and  $720\text{ cm}^{-1}$ . Our results tally with the results of Hummel et al. and other authors,<sup>24,27</sup> and the following assignment can be made. The band between  $2970$  and  $2800\text{ cm}^{-1}$  result from the antisymmetric vibrations of the methylene groups together with symmetric one. The band at  $1745\text{ cm}^{-1}$  is due to the carboxyl group ( $\text{C}=\text{O}$ ). The third range between  $1500$  and  $1100\text{ cm}^{-1}$  belongs mainly to wagging vibration of methylene group and to the  $\text{C}-\text{O}-\text{C}$  and  $\text{C}-\text{C}$  stretching vibration. The fourth band, between  $1100$  and  $720\text{ cm}^{-1}$ , belongs to rocking vibrations of the methylene groups and also chain-stretching vibrations involving the ester groups.

A typical  $^1\text{H-NMR}$  spectra of PVPR and PVA are presented in Figures 2(a) and 2(b). The signals observed at  $1.3$ – $1.9$  and  $4.2$ – $4.5$  ppm are due to methylene ( $-\text{CH}_2-$ ) and methine ( $-\overset{\text{H}}{\underset{|}{\text{C}}}-$ ) protons, respectively. The signals at  $0.9$  ppm appears due to the methyl ( $-\text{CH}_3$ ) proton, confirming the formation of the ester.<sup>23</sup>

TABLE I  
Characteristics of the Assam Crude Oil Collected from OIL, Duliajan

Physical properties	Value
Sp. gr. at $15^\circ\text{C}$ (g/mL)	0.8710
API gravity	31.0
Pour point ( $^\circ\text{C}$ )	+ 33
Kinematic viscosity at $40^\circ\text{C}$	3.95
Wax content	15.0
B.S & W	Trace

From GPC analysis, the weight-average molecular weight ( $M_w$ ) of the ester was found to be  $30,000$  relative to polystyrene standard of molecular weights  $1.8 \times 10^4$ ;  $498,000$ ;  $110,000$ ;  $20,400$ ;  $10,300$ ;  $4000$ ; and  $2100$ . Intrinsic viscosity ( $\eta$ ) of the polymer was found to be  $1.3\text{ dL g}^{-1}$ .

Percentage of unconverted hydroxyl groups in the ester was estimated by acetylation process. The result indicated that 94, 90, 86, 82, and 78% of the hydroxyl groups of PVA had been converted to ester groups<sup>28</sup> when the reaction time was 24, 22, 20, 18, and 16 h, respectively. The maximum extent of esterification was found to be 94% which is also confirmed from NMR data. The extent of the esterification reaction was calculated from the integrals of the various NMR resonance. The relative abundance of each proton calculated from the normalized integration indicates the extent of reaction in homogeneous esterification.<sup>23</sup> The comparison of methyl protons at  $0.9$  ppm and methylene protons at  $1.3$ – $1.9$  ppm yields a ratio of about  $1 : 1.25$  when compared with the expected  $1 : 1.33$  value. The ratio of the methine proton to methyl protons as calculated from experimental value is  $1 : 1.41$  when compared with the expected  $1 : 1.5$  value. So, the extent of esterification is around 94%.

The PVPR was soluble in a number of organic solvents like DMF, DMSO, dioxane, ethanol, chloroform, glacial acetic acid, tetrahydrofuran, etc. It was also sparingly soluble in benzene and toluene at  $40^\circ\text{C}$ . When PVPR with 94% conversion was tested as a flow improver at various concentration ranging from  $100$  to  $500$  ppm (Table II) on crude oil with physical

TABLE II  
Comparison of PVPR with Commercial Flow Improver on the Duliajan Crude Oil with Different Dosages

Dosages (ppm)	Pour Point ( $^\circ\text{C}$ )					Commercial flow improver
	PVPR with different degree of esterification (%)					
	94	90	86	82	78	
100	+ 27	+ 27	+ 30	+ 30	+ 33	+ 21
200	+ 27	+ 27	+ 30	+ 30	+ 33	+ 21
300	+ 24	+ 24	+ 27	+ 27	+ 33	+ 18
400	+ 24	+ 24	+ 27	+ 27	+ 33	+ 18
500	+ 24	+ 24	+ 27	+ 27	+ 33	+ 18

properties (mentioned in Table I), the pour point of the crude oil was found to be depressed only by 9°C compared to that of patented flow improvers like EC4242, which lowers the pour points of the same crude oil by 12–15°C at about the same concentration.<sup>29</sup> The product with less percentage of esterification reduces the flow improver quality of the PVPR and is shown in Table II.

Since PVPR contained unreacted 6% —OH group, it is less efficient than the commercial flow improvers. The efficiency of PVPR is expected to go up if the conversion becomes 100%. However, the full conversion is still elusive.

From the DSC studies (Fig. 3), the glass transition temperature,  $T_g$ , was found to be in between 29 and 58°C. The crystallinity of PVPR was found at 19.98%.

To check the thermal stability of the ester, the TGA and DTG curves (Fig. 4) were recorded in air. From DTG curves, it was observed that the ester decomposed in three stages.<sup>30</sup> The decomposition temperatures were determined by the intersection of the tangent to the steepest part of the TGA curve with its base line. The first-stage degradation was because of the removal of H<sub>2</sub>O from neighboring pairs of unconverted hydroxyl groups<sup>31</sup> as well as due to cleavage of the ester groups of the ester. The initial decomposition temperature (IDT<sub>1</sub>) for first stage of the PVPR was 270°C. The second-stage decomposition was because of the removal of CO, CO<sub>2</sub>, hydrocarbons, etc.<sup>32–35</sup> from the ester. The initial decomposition temperature (IDT<sub>2</sub>) for the second stage of the ester was 450°C. The third-stage decomposition was because of the production of carbon at temperature above 550°C. Integral procedural decomposition temperature (IPDT)<sup>36</sup> was found to be 410°C.

The method may lead to the synthesis and development of poly vinyl acetals, poly vinyl ethers, and other

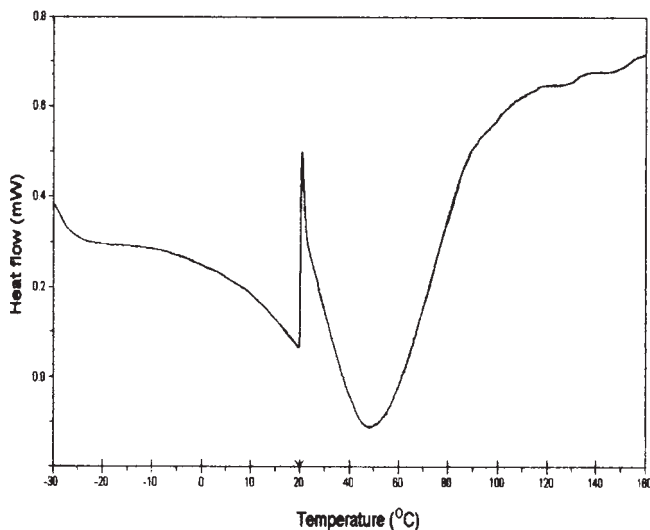


Figure 3 DSC curve of PVPR.

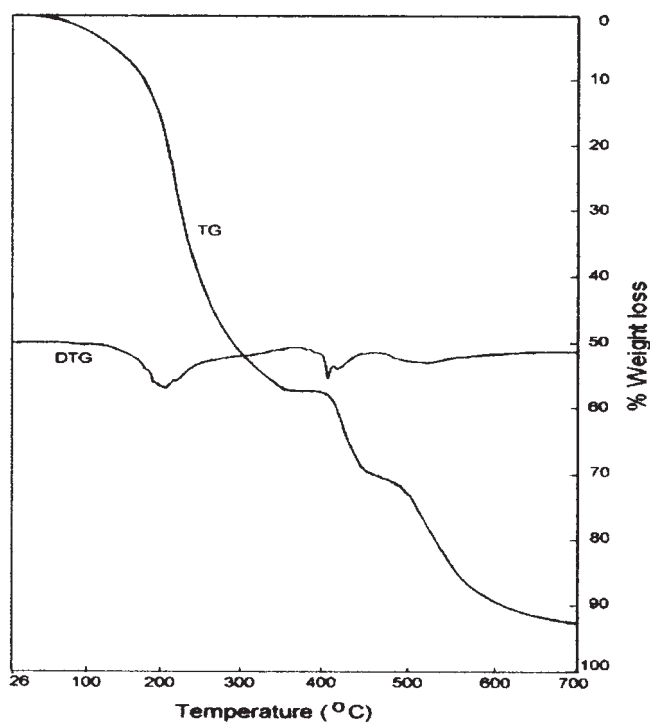


Figure 4 TGA and DTG curve of PVPR in air at a heating rate of 10°C/min.

commercially important chemicals from PVA. However, 100% conversion of all the hydroxyl groups into propionate groups is still elusive.

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## References

- Harrison, S. A.; Wheeler, D. N. *J Am Chem Soc* 1951, 73, 839.
- Rosen, I.; McCain, G. H.; Endrey, A. L.; Sturm, C. I. *J Polym Sci A-1* 1963, 1, 951.
- Terada, K.; Myazaki, H.; Maruyama, H. *Jpn. Pat.* 26,438,702 (1992).
- Watanabe, S.; Ichimura, K. *J Polym Sci Polym Chem Ed* 1982, 20, 3261.
- Tsudab, M. *Makromol Chem* 1964, 72, 174.
- Kato, M.; Ichijo, T.; Ishii, K.; Hasegawa, M. *J Polym Sci A-1* 1971, 9, 2109.
- Shibatani, K.; Fujii, K. *J Polym Sci A-1* 1970, 8, 1647.
- Minamino, H. *Jpn. Pat.* 06,65,311 (1992);
- Marvel, C. S.; Denoon, C. E. *J Am Chem Soc* 1938, 60, 1048.
- Ferrel, R. E.; Olcott, H. S.; Fraenkel-Conrat, H. *J Am Chem Soc* 1948, 70, 2101.
- Ashida, K. *Kobunshi Kagaku* 1953, 10, 117.
- Mishra, M. K.; Saxton, R. G. *U.S. Pat.* 5,834,408 (1998).
- Koch, P. *U.S. Pat.* 5,726,136 (1998).
- Gore, R. H.; O'Mara, J. H. *U.S. Pat.* 5,312,884 (1994).
- Illyckyj, S.; Tiedje, J. L.; *Ger. Pat.* 1,162,630 (1964).
- O'Neil, T. *J Polym Sci A-1* 1972, 10, 569.
- Chetri, P.; Islam, N.; Dass, N. N. *J Polym Sci Polym Chem Ed* 1996, 34, 1613.
- Kamani, M. M.; Parsania, P. H. *J Polym Mater* 1995, 12, 217.

19. Mann, F. G.; Saunders, B. C. *Practical Organic Chemistry*; Longmans: London, 1974; p 450.
20. Freeman, E. S.; Carroll, B. *J Phys Chem A* 1958, 62, 394.
21. *IP Standards for Petroleum and its products, Part 1*; The Institute of Petroleum: London, 1966; p 67.
22. Macmillan, N. *An Advanced Organic Laboratory Course*; Longmans: New York, 1972; p 10.
23. Chetri, P.; Dass, N. N. *J Appl Polym Sci* 1996, 62, 2139.
24. Chetri, P.; Dass, N. N. *Polymer* 1996, 37, 5289.
25. Haslam, J.; Wills, H. A. *Identification and Analysis of Plastics*; Van Nostrand and Company: Princeton, NJ, 1965; p 375.
26. Hummel, D. O.; Holland-Moritz, K.; Zoschke, E.; Hepple, P. *Molecular Spectroscopy*; Institute of Petroleum: London, 1972; p 301.
27. Fujii, K. *J Polym Sci Part D: Macromol Rev* 1971, 15, 477.
28. Chetri, P.; Dass, N. N. *J Polym Mater* 1998, 15, 51.
29. BhaskaraRao, B. K. *Modern Petroleum Refining Processes*; Oxford & IBH: London, 1984; p 152.
30. Beachell, H. C.; Fotis, P. *J Polym Sci* 1951, 7, 353.
31. Vasile, C.; Caluganu, E. M.; Bodonea, S. F. *J Polym Sci* 1981, 19, 897.
32. Ballistreri, A.; Foti, S.; Montaudo, G.; Scamporrino, E. *J Polym Sci Polym Chem Ed* 1980, 18, 1147.
33. Chatfield, D. A. *J Polym Sci Polym Chem Ed* 1983, 21, 1681.
34. Chetri, P.; Dass, N. N. *J Appl Polym Sci* 2001, 81, 1182.
35. Chetri, P.; Dass, N. N. *J Polym Mater* 1998, 15, 155.
36. Doyle, C. D. *Anal Chem* 1961, 33, 77.