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paper

A facile pathway to polyurea nanofiber fabrication and polymer morphology control in copolymerization of oxydianiline and toluene diisocyanate in acetone

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Precipitation polymerization of toluene diisocyanate and 4,4'-oxydianiline was carried out in acetone. At 1.0 wt% monomer concentration and 30 ºC for the polymerization temperature, polymers of different morphologies were obtained depending on the ways of agitation. Under mechanical stirring, rope-form polymer was obtained at low stirring rate and aggregate of granular polymer was observed with stirring rate at 600 r/min or higher; whereas polymer nanofibers were observed with quiescent polymerization and reciprocating shaking. Under quiescent polymerization with monomer concentration at 1.0 wt%, influence of polymerization temperature on the morphology of the polymer was studied. It was found that spherical particles were formed at 0 ºC, whereas fibrous polyurea was observed at 30 ºC or higher. Study on the influence of the monomer concentration at 30 ºC revealed that nanofibers were obtained at 2.0 wt% of monomer concentration or lower; and spherical particles were formed with higher monomer concentration. The basic properties of the polymers were characterized. This paper provides a novel and facile pathway to the fabrication of a novel type nanofiber of polyurea based on toluene diisocyanate and 4,4'-oxydianiline.

Introduction

Nanofibers, while there is some discussion on their exact definition, are commonly defined as fibers with diameters less than 100 nanometers.[1] In the nonwovens industry, the consensus has been that nanofibers include fibers as large as 1000 nm in diameter.[2,3] As one dimensional nano-materials of special structure, nanofibers are featured by huge specific surface, large length-diameter ratio, very high porosity and improved physico-chemical properties. Nanofibers have been extensively studied and can be applied in a great variety of fields,[3-32] including for instance biomedical applications,[6-14] sensors,[14-19] filters and functional membranes for separation of submicron particles,[20-22] absorbent in water treatment[23-25] and electronic devices[26-30] etc.

As for most high performance materials, the nature of nanofiber materials can be inorganic (often doped with rare earth metals),[15,32-41] polymeric[1-4,6-14,16,31] or their hybrid.[4,19,24,25,30,43] In comparison to inorganic materials, polymeric materials have a much greater design flexibility, because practically unlimited number of monomers can be designed. By copolymerization of these monomers and by chemical modification of their polymers[12,25] thus obtained, combined with the development in processing technologies,[1,2,6,44-47] one will have unlimited possibility in polymer structure design and achieve therefore different morphologies with adjustable properties. Nevertheless, the common processes for nanofiber fabrication remain quite sophisticated, involving usually delicate operations of multi-steps (for instance, electrospinning, solution or melt blown, self-assembly, template synthesis, phase separation or Islands-in-sea type bicomponent spinning model),[1,44-46] albeit relatively simple protocols have been reported. Mao *et al.*,[48] for instance, claimed that nanowires of poly(*N*-methylaniline) were achieved in oxidative polymerization of *N*-methylaniline using ammonium persulfate as oxidizing agent in the essential presence of cetyl trimethylammonium bromide. Tang *et al.*, in a series of reports,[49-51] reported preparations of nanotubes or nanofibers, based on chloro-substituted cyclotriphosphazene (HCCP) and 4,4'-sulfonyldiphenol (BPS), through an in-situ formed template of triethylammonium chloride (TEACl). In one paper,[49] crosslinked nanotubes were prepared through polymerization of HCCP with BPS followed by removal of nano-sized rodlike crystals TEACl. In other studies based on the same polymerization, nanofibers were obtained by adjusting the composition of a binary solvent acetone-toluene[50] or by control of the rate of polymerization.[51] In these cases, a supplementary step for removal of TEACl template was necessary.

Recently, we have been focusing our research on polyurea (PU) syntheses using isophorone diisocyanate with water or amines. Uniform polyurea microspheres[52,53] have been prepared with high yields; Core-shell and hollow microspheres were also achieved with addition of triethylene tetramine in a second step of polymerization to form a shell of crosslinked PU.[54] With toluene diisocyanate (TDI) instead of isophorone diisocyanate as the monomer,[55,56] porous PU was also obtained. However, when TDI was copolymerized with 4,4'-diaminodiphenyl ether (ODA, abbreviated from its alias 4,4'-oxydianiline) in acetone in the absence of water, nanofibrous PU with diameter of about 80 nm was observed with monomer concentration at 2 wt% or lower. In contrast to the common processes for nanofiber fabrication (electrospinning, solution or melt blown, self-assembly, template synthesis, phase separation or Islands-in-sea type bicomponent spinning model),[1,44-46] this provides a novel pathway to the fabrication of a novel type of PU nanofibers. Influences of the polymerization conditions were studied to optimize the production of this PU nanofiber.

Experimental

To a glass bottle of 120 mL capacity was charged 99 g of acetone (AR grade, Fuyu Chemicals, Tianjin), followed by addition of TDI (a mixture of 2,4- and 2,6- substituted isomers, CP grade, Keju new materials, Beijing) and ODA (CP grade, Aladdin, Shanghai) under gentle shaking. The amounts of TDI and ODA were controlled the way that TDI/ODA molar ratio was at 1.0. The bottle was sealed off and shaken by hand to make a homogeneous and clear solution, and the polymerization proceeded under quiescent condition (with the reactor standing still without any stirring or shaking) at 30 °C. Alternatively, the bottle reactor was located into a water bath at 30 °C (temperature for all polymerization except otherwise indicated) and polymerized for 4 h with reciprocating shaking or mechanical stirring. The polymerization was also carried out with varied monomer concentration and at different temperature. At end of the polymerization, samples were taken and centrifuged for 5 min at 12,000 r/min. The solid separated was rinsed twice with acetone prior to drying up at 80 °C for 6 h. The supernatant was sampled to obtain the low molecular polymers remaining soluble in acetone. Monomer conversion was calculated based on the solid separated by centrifugation and that in the supernatant.

The morphology of the product was examined using scanning electron microscopy (SEM, Hitachi S-2500). Thermal gravimetry analysis (TGA) was done using Diamond TG/DTA of Perkin Elmer instrument and differential scanning calorimetry (DSC) were done using Mettler Toledo SDTA-851 instruments. Infrared analysis done on an instrument of Bruker Vertex 70 FTIR spectrometer with the sample compressed in pellets of KBr.

Results and discussion

The polymerization and polymer structure are schematized in Fig. 1. Upon polymerization, polymers with higher degree of polymerization precipitated out. The content in the bottle reactor, initially a clear solution, turned turbid. By analysis of the homogeneous supernatant after centrifugation, an amount of involatile solid was collected, which was attributed to the oligomers of low degree of polymerization (soluble polymer). Monomer conversion was obtained based on the amounts of the precipitated and the soluble polymers (Table 1). The data show that all monomers were converted to polymer within 4 h of polymerization. The amount of the soluble polymer at low monomer concentration was significant, and this amount was decreasing with increased monomer concentration, which indicates that precipitation was enhanced with high monomer concentration because this will increase the polymerization rate and also the possibility of the oligomers to meet each other.

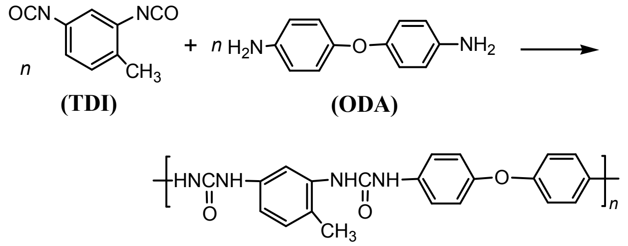

Fig. 1 Chemical equation for copolymerization of TDI and ODA

Table 1 Yields of polymers and monomer conversion in copolymerization of TDI and ODA (molar ratio at 1) under quiescent condition at 30 °C

Monomer concentration (wt%)	Soluble oligomers (wt%)	Precipitated polymer (wt%)	Monomer conversion (%)
0.5	44.0	56.0	100
1.0	23.2	76.0	99.2
2.0	22.0	77.1	99.1
3.0	15.3	83.3	98.6

Influence of agitation methods on polymer morphology

The copolymerization was then carried out using TDI (0.4655 g, 0.267 mmol) and ODA (0.5345g, 0.267 mmol) in 99 g of acetone at 30 ºC either under mechanical stirring (at 100 r/min), or with reciprocating shaking in a water bath, or with the reactor bottle standing still without any shaking or stirring (namely, quiescent polymerization). The products were examined under SEM and selective photos are presented in Fig. 2.

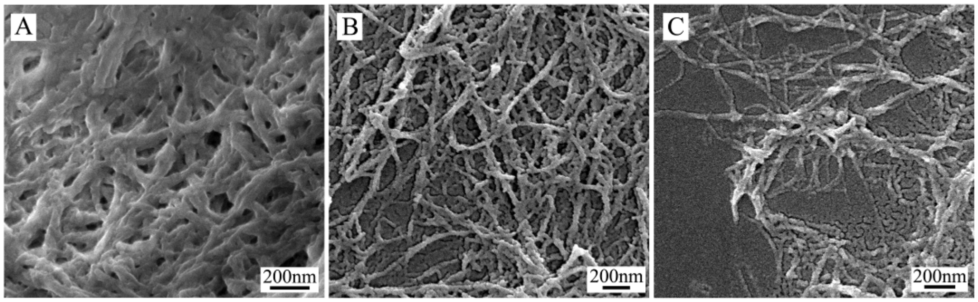

Fig. 2 Nanofibers obtained under different experimental conditions (A, Mechanical stirring at 100 r/min; B, Reciprocating shaking at 120 osc/min and C, Quiescent condition with the reactor standing still without shaking or stirring)

Fig. 2 shows clearly that fibers with diameter of about 100 nm were formed under mechanical stirring (Fig. 2A), and these fibers were seriously interlocked; whereas with the polymerization under shaking at 120 osc/min (Fig. 2B) or under quiescent condition (Fig. 2C), finer nanofibers than those obtained under mechanical stirring were observed, with their diameters varied from far below 100 nm to about 100 nm. In addition, the polymerization was also carried out with reciprocating shaking speed varied from 100 osc/min to 150 osc/min, no perceptible difference was observed under SEM, which indicates that the fiber formation was not significantly affected by shaking speed.

Based on the chemical structure of the resulting polymer (Fig. 1), which is basically consisting of aromatic rings with inserted carbamido units, one can conceive that the polymer chains must be very rigid. The flexibility of the polymer is largely limited, the solubility in acetone is low. The oligomers are therefore precipitated out at quite low degree of polymerization. Under such circumstance, the growing polymer chains at low degree of polymerization must be very sensitive to exterior stimulus such as stirring or shaking, which will accelerate the precipitation of growing chains by break down the fragile equilibrium of the oligomers when they reach or are close to the critical chain length[57] where they become insoluble. It is conceivable that these chains propagate at two terminals owing to the step-polymerization mechanism, and the resulting polymers are usually one dimensional (1D). Any single oligomer chain may encounter other chains during their growing up and these chains entangle together to form 1D nanofibers as shown in Fig. 2. Obviously, the stirring or shaking will enhance the probability for the growing chains to encounter and to form nanofibers with more chains entangled, leading to the formation of nanofibers with larger diameter in comparison with those prepared under quiescent polymerization as seen in Fig. 2A. Monomer concentration affects also polymer molecular weight and its distribution. It is believed that the influence of these factors may not be significant knowing that monomer concentration was quite low in all the polymerization. In fact, reliable testing is not available because the polyurea is not soluble in all tested solvents.

Polymerization temperature and nanofiber formation

The influence of polymerization temperature on nanofiber formation was then studied under quiescent polymerization with 1.0 wt% of monomer concentration and polymerization temperature varied from 0 ºC to 70 ºC. The resulting polymers were examined under SEM and selective pictures are given in Fig. 3.

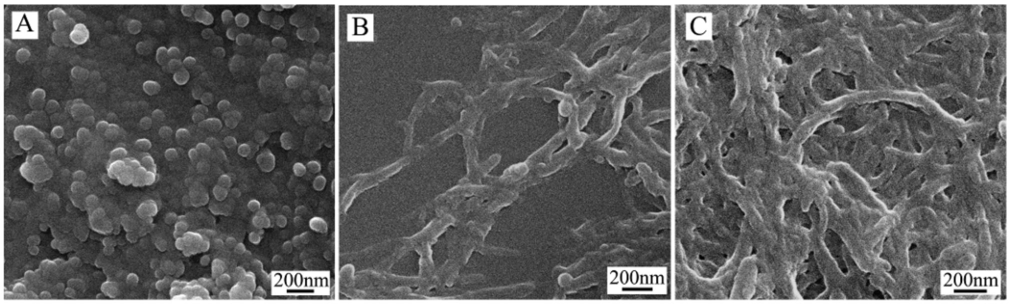

Fig. 3 SEM pictures of the polymers prepared at different polymerization temperature with monomer (TDI, ODA) concentration of 1.0 wt% (TDI/ODA molar ratio at 1) under quiescent condition (0 ºC, A; 30 ºC, Figure 2C; 50 ºC, B; 70 ºC, C)

Fig. 3 shows clearly that aggregated polymer spheres were observed with the polymerization temperature at 0 ºC; whereas nanofibers were formed with the polymerization temperature at 30 ºC or higher. In addition, the nanofibers became thicker with higher polymerization temperature. At lower temperature, the polymerization rate was slower, and the oligomer chains less flexible. With increased temperature, polymerization rate must be enhanced because of high diffusion rate for monomers and oligomers; the polymer chains must be also more flexible and easy to merge together, leading to formation of larger nanofibers in diameter. According to the relationship ΔG=ΔH-TΔS, a higher temperature leads also to a lower ΔG, which allows a higher solubility of the polymer and promotes the formation of the polymer of higher molecular weights prior to precipitation. Upon precipitation, the longer rigid-chain polymer has the tendency to form the observed fibrillar structure as shown in Fig. 3.

Monomer concentration and nanofiber formation

With the polymerization temperature fixed at 30 ºC under shaking at 150 osc/min, the polymerization was also carried out with different monomer concentration. SEM photos of the polymers are presented in Fig. 4.

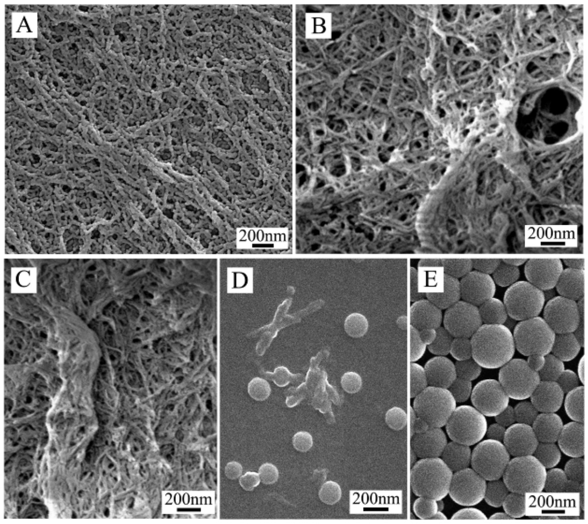

Fig. 4 Morphology of the polymers prepared at 30 ºC under reciprocating shaking (150 osc/min) with varied monomer concentration (by wt%. 0.5, A; 1.0, B; 2.0, C; 3.0, D and 5.0, E.)

From Fig. 4, a dramatic transition of the polymer morphology from nanofibers to microspheres is clearly seen with varied monomer concentration. With monomer concentration at 2.0 wt% or lower, polymer nanofibers were formed; whereas polymer spheres, with presence of some polymer rods, were formed at 3.0 wt% of monomer concentration, and only polymer spheres were present when monomer concentration was increased to 5.0 wt%.

As discussed above, the polymerization was started in acetone to form the primitive oligomers, which continued to grow at their two terminals to form 1D polymer chains, which would most likely remain as extended 1D polymer chains even after they reached their critical length owing to their rigidity. These polymers would appear as nanofibers if most of them did not encounter other growing chains until they had grown long enough to have a fiber form. At this stage and after wards, the fiber-shape polymers would remain as is even some of them merged or adhered together with extended polymerization time. However, the possibility of the merge and combination of the growing polymer chains was largely increased with increase in monomer concentration. At 3.0 wt% for instance, it is likely that most of the growing oligomers encountered a large number of their analogues before they were grown long enough to have a fiber-shaped polymer chains, prior to reach their critical length for example. In this case they would form primary particles like in common precipitation polymerization.[51,52,58,59] Once the primary particles formed, their fragile stability was provided by the growing chains with one end bonded to the surface and protected them from collision and eventual aggregation. The growth of the particles was assured either by polymerization of monomers with the oligomers adsorbed on the surface of the particles, or by direct polymerization of the monomers with the reactive groups on the same surface, keeping therefore the polymer spheres in their form up to the end of the polymerization. It is obvious that monomer concentration is playing a critical role in the control of the polymer morphology in this polymerization.

Polymerization in acetonitrile as the solvent

The polymerization was also carried out, with varied monomer concentration of 0.5, 1.0, 2.0 and 5.0 wt%, in acetonitrile instead of acetone at 30 °C in order to see how the morphology was changed in different solvent. It was found that polymer microspheres, of quite large size with high size distribution, were obtained in all cases, and no any fibrous polymer was observed under microscope (Fig. 5). This is in sharp contrast with the results obtained using acetone as the solvent.

To tentatively understand the results, the solubility parameters (SP) of the monomers, the solvents used and those of the resultant polyurea were collected and listed in Table 2. From this table, one can see clearly that, while the total SP of the two monomers (δ_M) are sitting between that of acetonitrile (δ_{AN}) and that of acetone (δ_{AT}), (i.e. $\delta_{AN}>\delta_M>\delta_{AT}$); the total SP of the polyurea (δ_P, 24.6 MPa$^{1/2}$) is exactly the same as that of acetonitrile δ_{AN}. The equality of the SP values for acetonitrile and the polyurea indicates that the polyurea was of better solubility in acetonitrile than in acetone. At the same time, the slightly higher SP of acetonitrile than polyurea also indicates that a higher interaction between the polymer chains and the molecules of the solvent in comparison with those of acetone. All these suggest that the chains of polyurea oligomers were better soluble in acetonitrile than in acetone, i.e. the chains of the oligomer formed in the earlier stage of the polymerization were less rigid in acetonitrile than in acetone, which makes them easier to adopt themselves to a spheroidal shape so that to have a lower surface energy for the system. Comparatively, the chains of polyurea formed in acetone will be more rigid, hard to adopt themselves, and they remained as rigid linear polymers, leading to the nanofibers.

The components of the total SP's, i.e. the SP owing to dispersion cohesive energy (δ_d), polarity (δ_p) and hydrogen bonding (δ_h), are also given in Table 2. δ_d values for both the solvents are almost the same; The δ_p values seem not playing great role because this value for the polyurea was extremely low in comparison with all the monomers and the solvents, which suggests that the polymer will have minimal interaction owing to polarization, likely due to the high symmetry in its molecular structure.

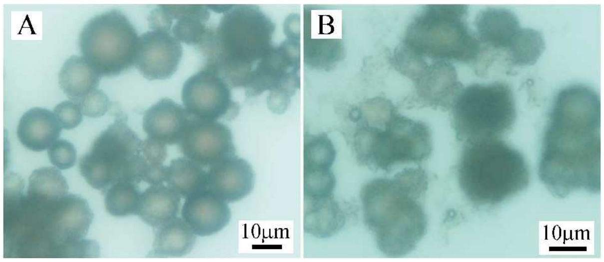

Fig. 5 Morphology of the polymers prepared at 30 ºC using acetonitrile as solvent under reciprocating shaking (150 osc/min) with varied monomer concentration of 1.0 wt% (A) and 5.0 wt% (B)

Table 2 Solubility parameters of the solvents, monomers and the polyurea

Solubility parameters (MPa$^{1/2}$)	δ	δ_d	δ_p	δ_h
Acetonitrile (AN)	24.6	15.3	18.0	6.1
Acetone (AT)	20.1	15.5	10.4	7.0
TDI	23.7	19.3	7.9	6.1
ODA[a]	22.8	18.4	7.0	11.5
P(TDI-ODA)[a]	24.6	22.6	2.9	9.3

a. The solubility parameters of ODA and P(TDI-ODA) were calculated using Beerbower method (Ref. 60); and the rest were taken from Ref. 61.

Characterization of the nanofibers

The polymer nanofibers, prepared at 30 °C with monomer concentration of 1.0 wt% under quiescent condition was subjected to Infra-red measurement (Fig. 6), which indicates that all typical peaks of adsorption expected for the polyurea were observed.[62] The peak related to isocyanate group (-NCO) at 2264 cm^{-1}, observed in TDI monomer, practically disappeared in the nanofibers, and at the same time enforced -NH peaks were largely observed at 3288 cm^{-1}, indicating the formation of the polyurea.

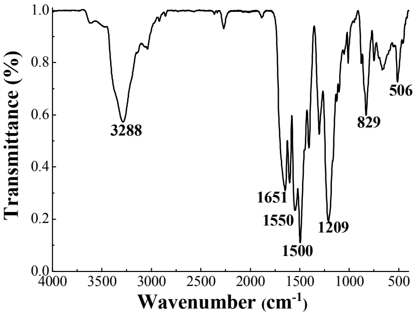

Fig. 6 FTIR spectra of polyurea nanofibers prepared at 30 °C with

monomer concentration of 1.0 wt% under quiescent condition

DSC test shown in Fig. 7 indicates that, apart from the slight fluctuation in the heat flow observed between 230 °C and 250 °C, there was no obvious glass transition temperature (Tg) within the temperature zone scanned from 30 °C to 300 °C, characteristic of polyurea attributed often to the presence of strong hydrogen bonding in the polymers.[62-65] Similar results have been observed in a number of studies on polyureas or polyurethanes,[62-66] and have been also interpreted by the heavy presence of hydrogen bonding, which makes most of the polymer segments "frozen" with partial crystallinity at the same time. The free movement of polymer chains and segments is severely restricted till the temperature of their degradation. Nevertheless, slight fluctuations of heat flow were in fact observed for some polyureas.[63-66] In a polyurea based on hexamethylene diisocyanate hexamethylene diamine, for example, Suresh et al. observed an exotherrmic peak around 250 °C,[65] a temperature just below the melting point of the polymer at about 285 °C. They attributed this exothemic peak to the arrangement of the polymer chains into a more ordered structure owing to increased mobility of the polymer chains at high temperature. Given the similarity of the thermal behavior and the polymers concerned, we suggest that the likely exothermal fluctuations observed at 230 °C and 250 °C (Fig. 7) may be also owing to a rearrangement of the polymer chains, leading to a more ordered structure and/or crystallized microdomains in the polymer. In the whole scanned temperature span, there was no any endothermic peak attributable to Tg was detected. Soon after the last exothermal heat fluctuation at 250 °C, the polymer started to degrade significantly from 260 °C, as shown by TGA test (Fig. 8). About 20% weight loss was detected at 300 °C, and about 75% of the polymer was decomposed at 360 °C. The residue was quite stable afterwards, and 15% of the initial weight remained up to 800°C. This demonstrates that this polyurea was of good thermal stability.

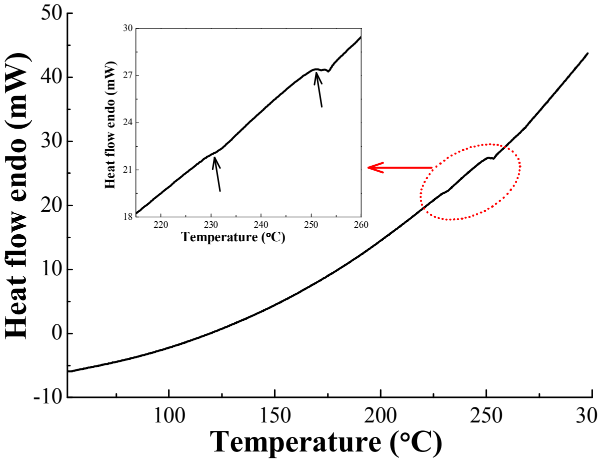

Fig. 7 DSC curve of polyurea nanofibers prepared at 30 °C with monomer concentration of 1.0 wt% under quiescent condition

The nanofibers as prepared were subjected to high speed agitation (1000 and 2000 r/min) after their preparation using a four-bladed turbine impeller. It was found that the fibrous morphology was retained after 30 min agitation, which indicates that the nanofibers were quite robust, high agitation could not destroy their structure and morphology. Tests were also done with purpose to find a solvent for the nanofibers using the same sample used for infrared test. To this end, 0.4 g of the nanofibers powder was dispersed into a bottle containing 100 g of the tested solvents, including acetic acid, toluene, acrylonitrile, *m*-cresol, tetrahydrofuran, the mixture of hydrochloric acid-acetone (1:1 by volume) and aqueous alkali solution (1.0 mol·L^{-1}). After hand shaking followed by treatment in an ultrasonic device for 3 min, the bottle was sealed off and located into a water bath at 70 °C and subjected to reciprocating shaking at 120 osc/min for 6 h. This test confirmed that the sample was not dissolved in any of the tested solvents, which indicates that the nanofibers are of good solvent-resistance.

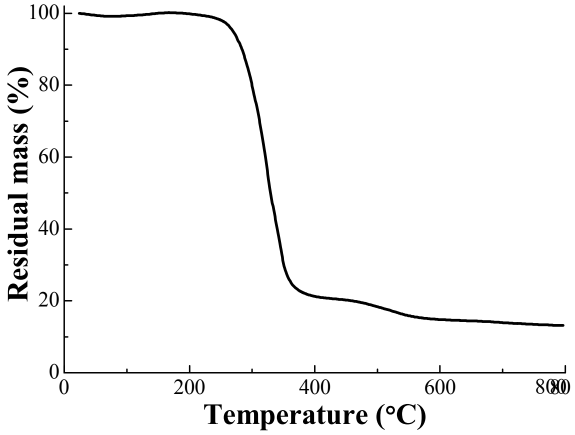

Fig. 8 TGA thermogram of polyurea nanofibers prepared at 30 °C with monomer concentration of 1.0 wt% under quiescent condition

Conclusions

Through precipitation polymerization of TDI and ODA at 30 ºC in acetone with monomer concentration at 1.0 wt%, polymers of different morphologies were obtained depending on the ways of agitation: polymer nanofibers were obtained under quiescent polymerization or with reciprocating shaking, rope-form polymer was obtained at low mechanical stirring rate, and aggregate of granular polymer was observed with mechanical stirring rate at 600 r/min or higher. With monomer concentration fixed at 1.0 wt% under quiescent polymerization, spherical particles were formed with polymerization at 0 ºC, whereas nanofibers was observed at 30 ºC or higher. This study revealed also that monomer concentration was playing also important role in controlling polymer morphology. With polymerization temperature fixed at 30 ºC under shaking, nanofibers were obtained when monomer concentration was at 2.0 wt% or lower; polymer spheres were formed at higher monomer concentration. Characterization of the polymers demonstrates that the polyurea as-prepared was of high thermal stability and excellent solvent resistant. We are currently working to find out a good solvent or solvent mixture in order to make yarn from the nanofibers through spinning so that to compare their properties with those of the nanofibers by one step polymerization.

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