Hyperbranched Poly([1,2,3]-triazole-[1,3,5]-triazine)s: An Unusual High Degree of Branching as an Effect of a Polyaddition Kinetics

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Summary: The results of the kinetic study of melt and solution polymerization at the 1,3-dipolar cycloaddition reaction of the AB_2 monomer – 2-azido-4,6-bis(prop-2-yn-1-yloxy)-[1,3,5]-triazine (ABPOT) are presented in this work as well as the results of the ^{13}C-NMR characterization of the obtained hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine)s. It is established, that the first-shell substitution effect during polyaddition process and unusual high degree of branching (up to 0.9) of polymers synthesized in melt are held.

Keywords: 1,3-dipolar Huisgen cycloaddition; degree of branching; hyperbranched; kinetics; poly([1,2,3]-triazole-[1,3,5]-triazine)s

Introduction

The tree-like molecular structure polymers are certainly among the most studied functional and special polymers today. [1–4] Hyperbranched polymers are an example of such interesting and topologically sophisticated macromolecules.[5] The reactions explored so far for the synthesis of dendritic polymers are numerous. It is necessary to note that the use of cycloaddition reactions offers more control over the polyreaction in comparison with addition reactions and other reactions of the polymer chemistry, and have the potential to form absolutely new structural units and also to achieve stereo-control and even unusual effects regarding the degree of branching.[2,6–8] However, ‘‘click’’-cycloaddition reactions of azide to alkynes began to be used for the preparation and functionalization of dendrimers, dendrimer-linear hybrids and hyperbranched polymers only few years ago.[9–14]

Recently, we have synthesized the novel hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine) by a 1,3-dipolar cycloaddition reaction of the crystalline AB_2 monomer – 2-azido-4,6-bis(prop-2-yn-1-yloxy)-[1,3,5]-triazine (ABPOT) (Figure 1) and have characterized the obtained polymers by solubility, IR-, ^{1}H-NMR-spectroscopy and SEC-data.[15,16]

The aim of this work was the kinetic study of solution and melt polymerization of ABPOT and characterization of the obtained hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine)s by NMR.

Kinetics of ABPOT Polymerization

The kinetic studies of ABPOT polymerization in melt and in DMF solution were performed on the isothermal MK 17–27 micro calorimeter.

The kinetic curves of ABPOT polymerization in melt at different temperatures (Figure 2) display that the reaction rate appreciably decreases because of diffusion problems at the last stage of polymerization, and a maximum reachable conversion depends on the reaction temperature (Table 1).

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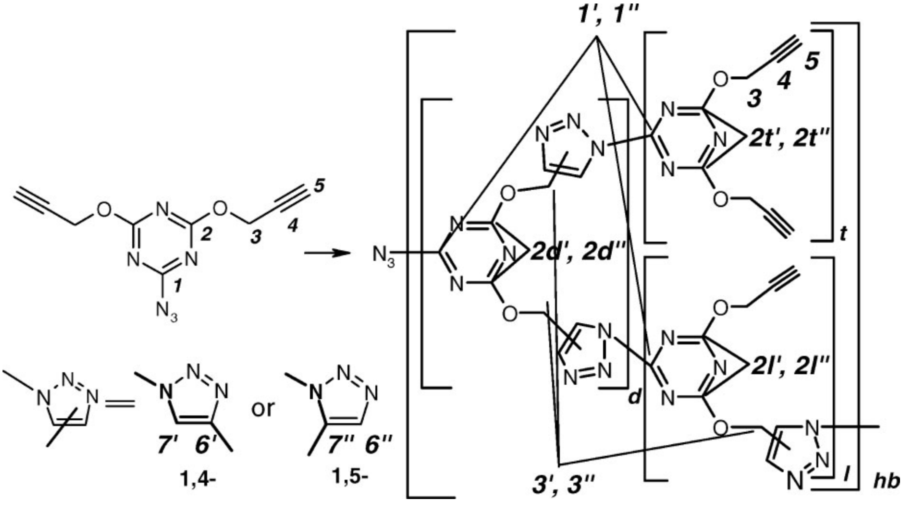

Figure 1.
Scheme of hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine) synthesis with the use of ABPOT monomer. *d* = branching, *t* = terminal, and *l* = linear units; *hb* = hyperbranched.

It is known, that the number average degree of polymerization ($\overline{DP_n}$) is inversely proportional to the difference between 1 and degree of conversion for polyaddition processes. So, this result is very important, because a temperature control during melt polymerization is a simple and environmentally friendly synthesis method of hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine)s with a quantitative yield and the control of polymerization degree, as was expected earlier.[16]

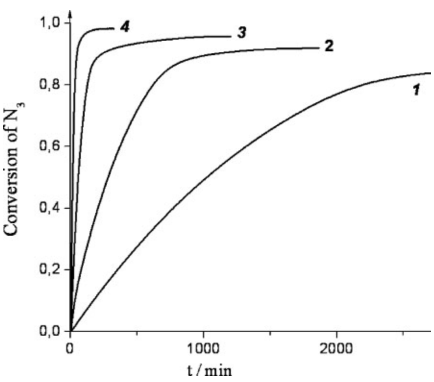

Figure 2.
Conversion of azido groups *vs.* polymerization time of ABPOT in melt at different temperatures: 46 °C (*1*); 60 °C (*2*); 80 °C (*3*); 100 °C (*4*).

The rate of ABPOT polymerization process should be written:

$$-d[\mathrm{N_3}]/dt = k[\mathrm{N_3}][A], \tag{1}$$

where $[\mathrm{N_3}]$ – concentration of the azides, (gram-equivalent)·l^{-1}; [A] – concentration of the triple bonds, (gram-equivalent)·l^{-1}.

As the $[\mathrm{N_3}]$ and [A] concentrations are different, Eq. (1) may be replaced by the integrated expression for a second-order reaction with nonequivalence of the functional groups concentrations:[17]

$$\frac{[A]}{[\mathrm{N_3}]} = \frac{[A]_0}{[\mathrm{N_3}]_0} e^{([A]_0-[N_3]_0)kt} \tag{2}$$

or

$$\frac{1}{[A]_0\text{-}[\mathrm{N_3}]_0} \ln\left(\frac{[\mathrm{N_3}] + ([A]_0\text{-}[\mathrm{N_3}]_0)}{[\mathrm{N_3}]}\right) = \frac{1}{[A]_0\text{-}[\mathrm{N_3}]_0} \ln\frac{[A]_0}{[\mathrm{N_3}]_0} + kt, \tag{3}$$

where $[\mathrm{N_3}]_0$, $[\mathrm{A}]_{\,0}$ – the initial concentrations of the functional groups, (gram-equivalent)•l^{-1}.

The evaluation of the kinetic data received at different temperatures in melt for the second-order kinetics (taking into account the nonequivalence of the functional groups concentrations) does not

Table 1.
The kinetic parameters of ABPOT polymerization in melt and in DMF solution.

Conditions	T,	conversion$_{max}$,	-ΔH_{polym},	$k_{eff} \times 10^6$, [c]		
	°C	%	kJ · mol^{-1}	·(mol · s)$^{-1}$		
				k_{in}	k_1	k_2
melt	46	85	195.5	0.9	1.1	2.3
	60	91–92	211.9	2.7	3.6	6.2
	80	96–97	222.3	16	19	32
	100	98–99	228.2	64	81	120
DMF solution	60 [a]					1.9
	80 [b]			10		12

[a] [ABPOT] = 0.29 mol · L^{-1}.
[b] [ABPOT] = 0.32 mol · L^{-1}.
[c] k_{in} = initial reaction rate constant; k_1 = reaction rate constant at the conversion degree less than 45%; k_2 = reaction rate constant at the conversion degree more than 50%.

show ideal linear behavior (Figure 3). The effective reaction rate constants (k_{eff}) increase almost twice at the conversion degree more than 45–50% (Table 1, Figure 3). This fact may be explained by a matrix self-catalysis with the generation of some special triazole cycle containing intermediate (in other words, by a first shell substitution effect – a reactivity of the ''second'' triple bond of the monomer increases after the ''first'' triple bond have reacted with azide).

Such peculiarity is not observed for the kinetics of ABPOT polymerization in DMF solution (Figure 4). The effective reaction rate constants (k_{eff}) are calculated from the curves (Table 1). A curvature after 4000 min at 80 °C or after 8000 min at 60 °C can be explained by an influence of side reactions occurred in polar solvents at heating on kinetics.

The activation energies of the polymerization (E_{akt}) in melt or in DMF solution are equal and average value is about 86–88 kJ/mol.

The kinetics of catalytic polymerization of ABPOT (at presence of Cu^{I}-salts) was not studied because of very high rate of a reaction at temperature more than 20 °C, large amount of side reactions proceeded during solution and melt catalytic polymerization, and a great enthalpy of reactions (as an example, $\triangle H_{polym}$ = - 420 kJ · mol^{-1}, reaction conditions T = 60 °C, DMF solu-

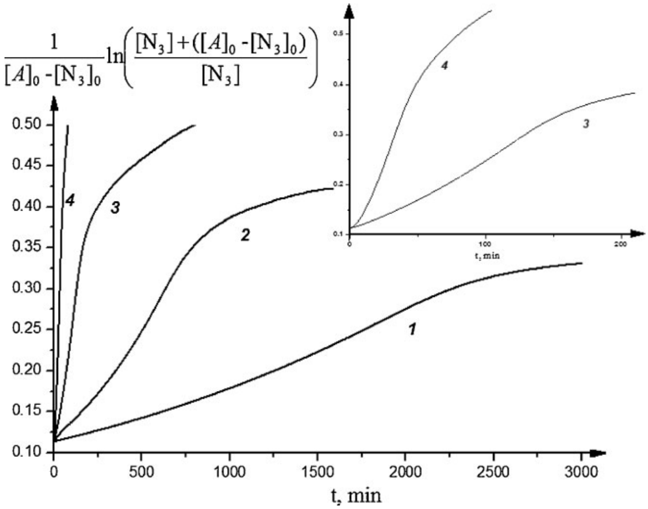

Figure 3.
The ABPOT polymerization in melt: *1* at 46 °C; *2* at 60 °C; *3* at 80 °C; *4* at 100 °C.

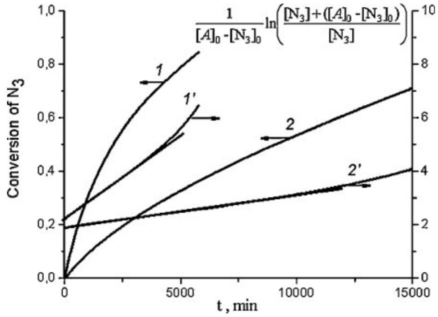

Figure 4.
The polymerization of ABPOT in DMF solution. Reaction conditions $T = 80\,^{\circ}C$, $[ABPOT] = 0.32\ mol \cdot L^{-1}$, (1, 1′); $T = 60\,^{\circ}C$, $[ABPOT] = 0.29\ mol \cdot L^{-1}$ (2, 2′).

tion, $[ABPOT] = 0.06\ mol \cdot L^{-1}$, $[CuCl] = 2.8 \cdot 10^{-3}\ mol \cdot L^{-1}$).

13C-NMR Investigations and Degree of Branching

Generally, the positive first shell substitution effects favor the second branching during hyperbranched polymers obtaining by AB_n-methodology. Therefore, we focused our attention on the determination of the degree of branching (*DB*) of the hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine)s synthesized in melt.

The quantitative ^{13}C-NMR measurements were performed on the Bruker Avance 300 SF NMR spectrometer operating at 75 MHz. DMSO-d6 was used as a solvent for the NMR experiments. TMS was used as an internal standard.

The obtained ^{13}C-NMR spectra show a decrease of peak intensity of carbon atoms belonging to the monomer, an appearance and a rise of new carbon signals correspondingly (Figure 5).

The most important region of the NMR spectra is the region between 172.5–171.5 ppm corresponded to the triazine carbon atoms. There are signals caused by carbons in the positions of 4 and 6 of triazine within moieties where both of B (i.e. $-O-CH_2-C{\equiv}CH$) groups have reacted to form triazoles (subscript *d*; *2d′*, *2d″*), occurring in *d*-units, within moieties with one of the propargylic group has reacted (subscript *l*; *2l′*, *2l″*), occurring in *l*-units, and within moieties with unreacted propagylic groups (subscript *l*; *2t′*, *2t″*), occurring in *t*-units.

The degree of branching was calculated by the equation [18]:

$$DB = \frac{2 \cdot D}{2 \cdot D + L} \approx \frac{2 \cdot D}{D + T + L} = \frac{2 \cdot \int_{172.4}^{172} I}{\int_{172.4}^{172} I + \int_{172.4}^{171.5} I}$$

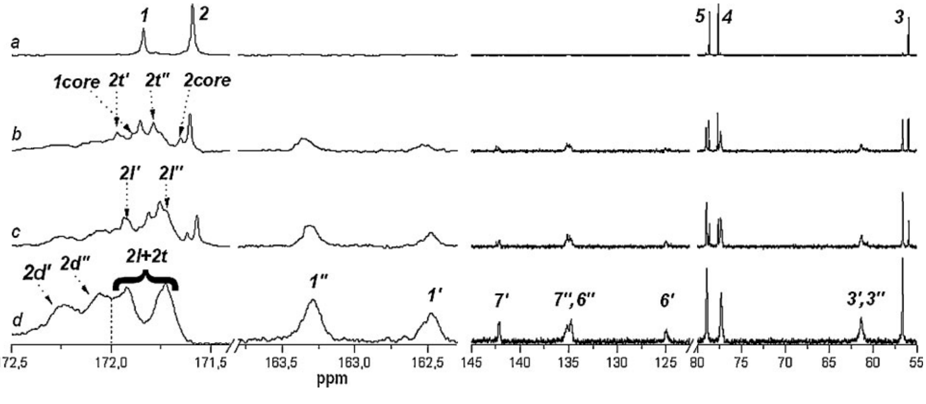

Figure 5.
Stack of ^{13}C-NMR spectra of the monomer ABPOT (a) and poly([1,2,3]-triazole-[1,3,5]-triazine)s obtained in melt with different degree of azido groups conversion: 66% (*b*), 78% (*c*), 98% (*d*).

On the basis of this equation we determined that *DB* of hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine)s depends on a degree of conversion: $DB = 0.87$ for the polymer with conversion of azide close to 98%, $DB = 0.65$ at 77% conversion, and $DB = 0.57$ at 66% conversion of azido groups correspondingly. This non statistical branching ($DB >> 0.5$) can be explained by an increase in reactivity of the ''second'' propargylic group after the ''first'' group have reacted with azide, i.e. by the first shell substitution effect through a matrix self-catalysis, as we have illustrated by kinetic results above. It is significant, that *DB* begin to increase rapidly at the second stage of melt polyaddition process when the effective reaction rate constants grow.

Conclusion

The kinetic laws for the ABPOT polymerization by a 1,3-dipolar cycloaddition in melt and in DMF solution are determined and degree of branching of the obtained poly([1,2,3]-triazole-[1,3,5]-triazine)s is established. The synthesis method for hyperbranched poly([1,2,3]-triazole-[1,3,5]-triazine)s in melt is confirmed by these investigations as a simple and environmentally friendly approach with the control of polymerization degree, degree of branching and with quantitative yield.

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