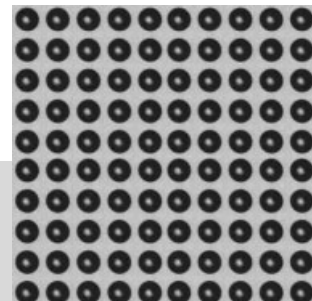


Inkjet Printing of Polymers: State of the Art and Future Developments**

By Berend-Jan de Gans, Paul C. Duineveld,
and Ulrich S. Schubert*



Inkjet printing is considered to be a key technology in the field of defined polymer deposition. This article provides an introduction to inkjet printing technology and a short overview of the available instrumentation. Examples of polymer inkjet printing are given, including the manufacturing of multicolor polymer light-emitting diode displays, polymer electronics, three-dimensional printing, and oral dosage forms for controlled drug release. Special emphasis is placed upon the utilized polymers and conditions, such as polymer structure, molar mass, solvents, and concentration. Studies on viscoelastic fluid jets and the formation of viscoelastic droplets under gravity indicate that strain hardening is the key parameter that determines the inkjet printability of polymer solutions.

1. Introduction

Inkjet printing is a familiar method for transferring electronic data to paper or overhead transparencies, and is nowadays present in nearly every office and household. In recent years, however, much effort has been invested in turning inkjet printing into a versatile tool for various industrial manufacturing processes, in order to accurately deposit minute quantities of materials. Examples include solder for microelectronics soldering, lubricants for micromechanical parts, and UV-curable resins for the manufacturing of entire micro-optical parts, such as waveguides, micro-lenses, and arrays thereof.^[1] Inkjet printing is also considered to be one of the key technologies in the field of defined polymer deposition, particularly in relation to the manufacturing of multicolor

polymer light-emitting diode (PLED) displays. The display is printed pixel-wise using solutions of differently colored electroluminescent polymers. Similarly, inkjet printing is used for the manufacturing of polymer electronics.^[2] Three-dimensional printing is a mold-free manufacturing technique that comprises inkjet printing of some pattern on a compacted layer of ceramic powder using a polymeric binder solution. The pattern represents a slice of a three-dimensional form. The printing process is repeated slice after slice to obtain the object, from which the unbound powder is then removed. Using polymer rather than ceramic powder as a substrate, three-dimensional inkjet printing is also used to fabricate oral dosage forms for controlled drug release. Finally, dilute solutions of ceramic particles plus a polymeric binder are used to produce three-dimensional structures by overprinting. It is surprising, however, that comparatively little information has been published on how inkjet printability of polymers correlates with polymer structure and molecular weight, concentration, and solvent used.

This review provides a collection of this knowledge, based on what is published in the scientific literature. We are aware that this represents a restriction; more information on polymer inkjet printing can be found in the patent literature, especially in relation to inkjet ink additives.^[3] The instrumentation available for polymer inkjet printing will be discussed briefly. Studies that relate inkjet printability of (polymer-containing) inks to their rheological properties are rare, but from studies in the closely related fields of vis-

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coelastic droplet formation dynamics and the stability of viscoelastic jets it can be inferred that small quantities of high-molecular-weight polymers can have a strong influence. Results relevant for inkjet printing will be discussed. Finally, the application of polymer inkjet printing to combinatorial material research, a high-interest area, will be considered. The current bottleneck in combinatorial polymeric materials research is the creation of polymer microarrays prior to characterization. We believe that inkjet printing may bridge this gap. In the past, inkjet-printed microarrays were used for the screening of luminescent materials,^[4] catalysts for carbon-nanotube synthesis,^[5] DNA-fragments, and

other bioactive molecules,^[6] but the authors are not aware of any similar activities in the field of polymer science.

2. Inkjet Printing Technology

In this section, an introduction to inkjet printing technology and the available instrumentation for polymer inkjet printing is given. For detailed information we refer to reviews covering the subject.^[7] Inkjet printers may operate either in continuous or drop-on-demand (DOD) mode. In continuous-mode inkjet printing, the ink is pumped through a nozzle to form a liquid



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jet. Uniformly spaced and sized droplets are obtained by imposing a periodic perturbation, leading to surface-tension driven jet break-up. Continuous-mode inkjet printing is mainly used for high-speed graphical applications such as textile printing and labeling. In all the applications we discuss in this review, drop-on-demand is the method of choice, due to its smaller drop size and higher placement accuracy. An acoustic pulse ejects ink droplets from a reservoir through a nozzle. The pulse can be generated either thermally or piezoelectrically. In a thermal DOD inkjet printer (or bubble-jet), ink is heated locally to form a rapidly expanding vapor bubble that ejects an ink droplet. Thermal DOD usually uses water as a solvent and may therefore impose restrictions on the number of polymers that can be printed using this technique, although non-aqueous thermal inks are available. Piezoelectric DOD inkjet printing on the other hand, relies on the deformation of some piezoelectric material to cause a sudden volume change and hence generate an acoustic pulse. Piezoelectric DOD is, in principle, suited to a variety of solvents.

The most crucial part of inkjet printing technology is probably the ink and its physical properties, in particular the viscosity and surface tension. The viscosity should be suitably low, typically below 20 mPa s. When too much kinetic energy is viscously dissipated no droplet is ejected. Eventual polymer solutions should therefore be sufficiently dilute. The shear rates involved in inkjet printing are, however, usually of the order 10^5 s^{-1} , hence shear-thinning may occur. For a given pressure wave at the nozzle, the lower the viscosity the greater the velocity and amount of fluid propelled forwards, which usually leads to the formation of long tails behind the head of the drop. The surface tension is responsible for the spheroidal shape of the liquid drop emerging from the nozzle. In practice, surface tension ranges from 28 mN m^{-1} (for, e.g., xylene), to 350 mN m^{-1} for a molten solder.^[8] Finally, the wetting behavior of fluid and nozzle material is of importance, as wetting of the nozzle outlet face results in spray formation. Droplet formation during inkjet printing as a function of fluid properties was also modeled numerically.^[9]

In principle, polymers can be printed from the melt when the complete inkjet system can be heated. This technology is used in graphical industry for printing waxes.^[10,11] Another possibility for inkjet printing of polymers is represented by the utilization of colloidal suspensions of polymer lattices, which has the advantage of presenting a high-molecular-weight polymer in a low-viscosity form. The latter possibility was demonstrated by Wong et al.^[12] In recent years the use of colloidal matter in the form of pigments in inkjet ink formulations has become more and more widespread, due to their superior light-fastness as compared to molecular dyes. However, when particle size becomes of the order of $1 \mu\text{m}$, printability problems may occur.^[13]

Numerous companies produce inkjet devices for everyday or industrial printing purposes. Their equipment can in principle be adapted for polymer printing—examples will be given in the next section—but specialized equipment is also on the

market. Instruments for polymer inkjet printing and requirements thereon were recently discussed in great detail from a combinatorial material science point of view.^[14] Here, only a short overview of manufacturers and the apparatus they produce will be given.

The Autodrop Platform from Microdrop is built around 8 glass nozzles running in parallel.^[15] The nozzle diameter can be varied between 30 and $100 \mu\text{m}$, allowing fluid dispensing on a picoliter scale, with frequencies of up to $2000 \text{ drops s}^{-1}$ per nozzle. The upper limit for the ink viscosity is 20 mPa s at operating temperature. A special print head is offered that can be heated to $150 \text{ }^\circ\text{C}$. Positioning accuracy in the *XY*-direction is $10 \pm 3 \mu\text{m}$. Two video cameras allow observation of drop formation and impact. A picture of the device is shown in Figure 1. The Nano-Plotter NP1.2 and NP2 from GeSiM,^[16] developed for the life sciences, and the Jetlab series from Mi-

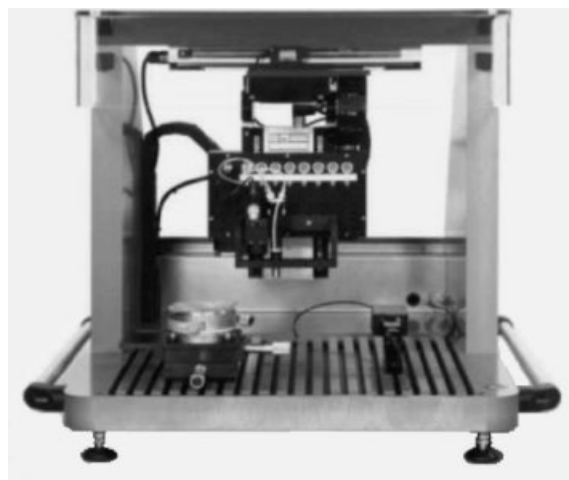


Figure 1. Microdrop Autodrop Platform (courtesy Microdrop GmbH, Germany).

crofab offer similar specifications.^[17] Part of the Jetlab series is the Polymer Jet print head, which can be heated to $220 \text{ }^\circ\text{C}$. The 80L and 140P Piezo Micro Deposition Systems by Litrex^[18] were exclusively developed for the manufacturing of PLED displays. Multi-nozzle inkjet print heads are used, containing several hundreds of individual nozzles.^[10]

A number of manufacturers developed (nano)dispensers for life-science applications.^[19,20] Their equipment is based on syringe pumps and micro-solenoid valves rather than on inkjet technology. Minimum amounts of tens of nanoliters can be dispensed. The Biochip Arrayer from Perkin Elmer is a hybrid device, using both inkjet and syringe pump technology.^[21] This combination has the advantage that the dispensed amount is always equal, even if the dispensed fluid contains particulate material, such as cells. The minimum dispensable amount is 325 pL .

3. Applications of Polymer Inkjet Printing

3.1. Manufacturing of PLED Displays and Liquid-Crystal Display Color Filters

In this section, the open literature about polymer inkjet printing will be reviewed, starting with the manufacturing of multicolor polymer light-emitting diodes or PLED displays. Monochromatic displays can be prepared by spin-coating, but the fabrication of multicolor displays requires a micro-patterning technique to locally deposit three differently colored electroluminescent polymers. At the moment, the most promising approach seems to be inkjet printing. An example of such a display is shown in Figure 2. The advantages of inkjet printing are its inherent flexibility, the ease of mass fabrica-

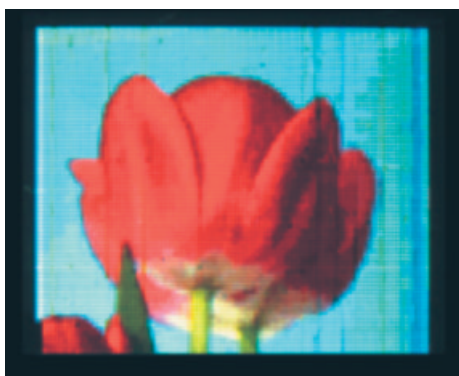


Figure 2. Multicolor 130 ppi PLED display (courtesy A. Giraldo, Philips Research, The Netherlands).

tion and the possibility of depositing very small amounts of material. A disadvantage is the restriction to low viscosities, and therefore low polymer concentrations.^[22] An overview of PLED display technology, including inkjet printing fabrication was recently given by Haskal et al.^[23]

Inkjet printing was used to create 200 μm diameter dots of polyvinylcarbazol (M_w 1.1×10^6 , 10 g L^{-1} solution in chloroform), using a Canon PJ-1080A color inkjet printer.^[24] The polymer was doped with various emitting dyes to obtain different colors. Bharathan and Yang^[25] produced the first PLED device using inkjet printing, a light-emitting logo. An aqueous solution of semiconducting poly(3,4-ethylenedioxythiophene) (PEDOT) was utilized as ink. The logo was then covered with a spin-coated polymer buffer layer, consisting of electroluminescent poly(2-methoxy-5-2'-ethylhexyloxy-1,4-phenylene vinylene). The PEDOT layer defined the emissive area. Dual color light-emitting pixels^[26] were fabricated by printing a 2 wt.-% aqueous solution of orange-emitting poly[5-methoxy-(2-propanoxy-sulfonide)-1,4-phenylene vinylene] (MPS-PPV) on a spin-coated film of blue-emitting poly[2,5-bis[2-(*N,N,N*-triethylammonium)ethoxy]1,4-phenylene] (PPP- NEt_3^+). In regions where the PPP- NEt_3^+ layer was doped with MPS-PPV, the pixel showed orange emission due

to energy transfer; otherwise blue light was emitted. An Epson Stylus II printer was used for the experiments. A significant step forwards was the fabrication of an active matrix red–green–blue (RGB) multicolor panel^[27] using a 0.3 wt.-% solution of a precursor of poly(*p*-phenylene vinylene) and a CFP-Mark II printer with a Seiko-Epson Stylus 3000 print head. To improve print resolution the 20 pL droplets (corresponding to a 33 μm diameter) were deposited between barriers made by photolithography, which is now the generally accepted route for display manufacturing. To prevent the droplets from flowing over the barriers they were treated with a CF_4 plasma to render the surface of the polyimide hydrophobic without changing the hydrophilic properties of the (inorganic) substrate. The important aspect of substrate wetting is discussed in more detail by Duineveld and co-workers, both in the case of printing between barriers^[22] and on a homogeneous substrate.^[28] In the latter paper the stability of an inkjet printed liquid line on a surface was investigated both experimentally and theoretically, as a function of surface properties and print head velocity. An aqueous solution of Baytron-P was used in the experiment, with a viscosity of 20 mPa s.

Kamiura et al.^[29] and Duineveld et al.^[22] both report on the inkjet fabrication of a true full-color 80 ppi active and passive matrix displays, using the PI-barrier technique for pixel definition. Much effort is currently being put into resolution improvement, recent work has seen an increase to 130 ppi by Seiko-Epson,^[30] and Philips,^[31] corresponding to a 66 μm pixel size. A schematic picture of such a display is shown in Figure 3. In order to offer sufficient tolerance to droplet landing errors, 8–14 pL droplets were used, corresponding to a 12–

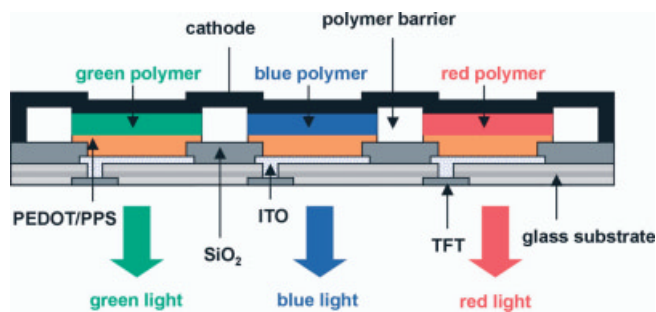


Figure 3. Schematic picture of a RGB multicolor PLED display. Green, blue, and red light-emitting polymers are printed between polymer barriers, on top of a conducting polymeric PEDOT/PPS layer. The anode consists of transparent indium tin oxide (ITO). Each pixel is addressed individually with a thin film transistor (TFT).

15 μm droplet radius. It has been shown that inkjet printing does not decrease the efficiency of the display.^[22] Another important aspect is display size; an increase to 17 in. (1 in. = 2.54 cm) was reported recently.^[32]

The ink is the key ingredient of this technology. The Philips group uses inks based on poly(*p*-phenylene vinylene) (PPV)

derivatives, containing 0.5–2% polymer by weight.^[33] Amongst others, tetraline, anisole, and *o*-xylene were used as solvents. Polymer addition influences inkjet printability through the elongational viscosity. The effect on drop formation is shown in Figure 4: (note the fluid filament connecting

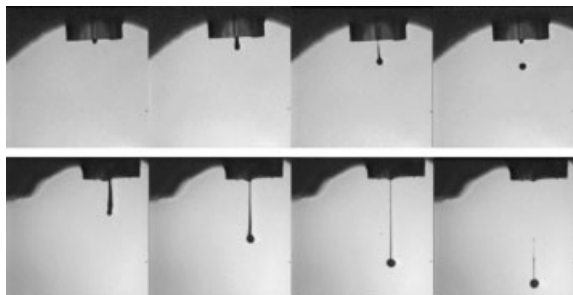


Figure 4. Stroboscopic images of droplets, produced by inkjet printing. The upper picture series shows a Newtonian fluid. The lower picture series shows the effect of an addition of a small amount of a high molecular weight polymer. Note the formation of a filament connecting drop and nozzle. The diameter of the droplet in the lower right image is 70 μm . (Permission for reprint from [34], courtesy Society for Information Display).

droplet with nozzle). Above a molecular weight of 300 000 (M_n) or 500 000 (M_w), the filament length increases such that no separate drops are formed. This surprising printability of high-molecular-weight PPVs was attributed to the stiffness of the PPV backbone. The elongation rate was estimated as $\dot{\epsilon} \approx 1/L(dL/dt) \approx v/L$ where v is a characteristic velocity and L a characteristic length scale.^[34] Using for L a 50 μm drop size, and assuming that v is a few meters per second, it is found that $\dot{\epsilon}$ is of the order 10^4 s^{-1} . Ink evaporation conditions and the spreading of polymer to the pixel edges are controlled by using mixtures of solvents with low and high boiling points, respectively.^[34] Alternatively, the substrate can be also heated.

The polymer film that remains after solvent evaporation should have a homogeneous thickness for good color uniformity. In general, when a droplet evaporates most of the solute is deposited as a perimeter ring. This is due to pinning of the contact line between droplet and substrate, which causes a capillary flow, replenishing liquid evaporating from the edge by liquid from the interior.^[35] Uniform deposits were obtained by using a very low vapor pressure solvent, e.g., dimethylsulfoxide (DMSO).^[36]

Another display-related field where inkjet technology is used, is the fabrication of color filters for liquid-crystal displays (LCDs). Here, every pixel is imprinted with inks containing differently colored dyes or pigments to create a multi-color display. Proof of the principle of inkjet-printed color filters was reported somewhat earlier than PLED devices.^[37] Recently a complete working thin film transistor (TFT)–LCD display with an inkjet-printed color filter containing acrylic polymers as binders was reported.^[38]

3.2. Organic Electronic Components and Circuits

Advances in the field of conducting polymers have opened the way for all-polymer electronic components and circuits. The advantage of polymers over conventional amorphous silicon-based technology is the limited number of processing steps, and therefore, the low cost. Currently, polymers are inferior to silicon with respect to switching speed. They are potentially useful when cost rather than speed is essential, e.g., in smart cards, electronics tags, and labels or sensors. Device construction methods were recently reviewed.^[39]

Thin lines of poly(3,3'-dipenthoxybithiophene) were inkjet-printed, becoming conducting after exposure to iodine vapor, using chloroform and trichloroethylene as solvents.^[40] The 1D structures became more homogeneous when printing more than one drop at each point. All-polymer thin film transistors or TFTs were fabricated with a combination of inkjet printing and spin-coating.^[41] A schematic picture of the transistor is shown in Figure 5. An aqueous solution of Baytron-P was used to print the electrodes. Baytron-P consists of a poly(styrene sulfonic acid) (PSS) backbone (with a M_w of the order

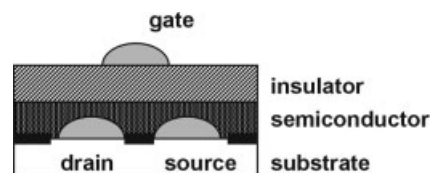


Figure 5. Schematic picture of inkjet printed all-polymer thin film transistor, as constructed by Siringhaus et al. [41]. Source and drain electrode, consisting of PEDOT/PPS are inkjet printed on a pre-patterned surface. Two spin-coated layers of semiconducting and insulating polymer respectively cover the electrodes. Finally the gate electrode is printed on top.

10^5) doped with conducting oligomeric PEDOT counter-ions. Printing resolution could be improved to 5 μm by patterning the substrate with alternating hydrophilic glass and narrow hydrophobic polyimide regions. Solvent inkjet printing forms via-hole interconnections, providing electrical contact between different layers. The upper polymer dissolves and upon drying of the solvent re-deposits on the sidewalls of the crater-like intrusion formed, again due to pinning of the contact line. Solvent is printed until the underlying, insoluble layer is exposed. An atomic force microscopy (AFM) picture is shown in Figure 6. Finally, the via-hole was filled with Baytron-P. Transistor-based inverter circuits were printed.^[42] Zhang et al. also claimed to have successfully inkjet printed an all-polymer transistor including poly(4-vinyl phenol) (PVP) and polythiophene.^[43] With a single-nozzle piezoelectric inkjet printer a solution of semiconducting poly[(9,9-dioctylfluorene)-*co*-bithiophene] (F8T2) in xylene was printed to fabricate transistors. The direction of printing of the semiconductor with respect to the source–drain had a con-

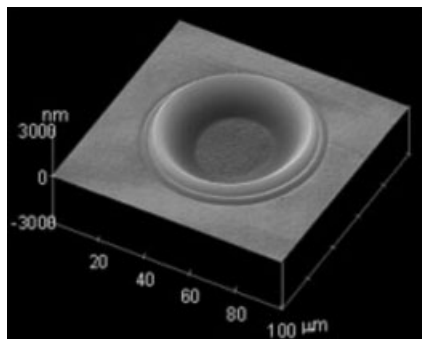


Figure 6. AFM picture of a via-hole interconnection created by Kawase et al. by deposition of solvent using inkjet technology. The polymer dissolves and upon drying of the solvent redeposits on the sidewalls of the crater-like intrusion formed. Solvent is printed until the underlying, insoluble layer is exposed. (Reprinted from [42b]. Copyright 2001 Wiley-VCH).

siderable influence on the transistor characteristics.^[44] Finally, Stutzmann et al. reported on the construction of polymer field-effect transistors, using inkjet printing for the coarse patterning of Baytron-P source–drain electrodes and spin-coating to deposit the semiconducting and insulating polymer layers.^[45] Solid-state embossing was used to produce the sub-micrometer features. The self-aligned gate electrode was inkjet printed on top, in an embossed hydrophilic groove (whereas the rest of the surface was rendered hydrophobic with a micro-contact-printed monolayer of octyltrichlorosilane).

An all-polymer capacitor and an RC filter were printed with an Epson Stylus Color 480 SXU inkjet printer,^[46] using Baytron-P and polyaniline as conducting polymers and poly(4-vinylphenol) (PVPh) as resistor. 1-Methyl-2-pyrrolidone was utilized as solvent in the latter experiment. Polytetrafluoroethylene could not be used as the resistor, since it clogs the printer nozzle easily. The same holds true for the use of ethanol and acetone as solvents for PVPh; they quickly evaporate to leave PVPh particles that block the printer nozzles. Selective electroless nickel-plating on a patterned polyelectrolyte multilayer substrate was demonstrated using a modified Epson Stylus Color 670 inkjet printer.^[47] This multilayer, consisting of alternating layers of polycations and polyanions, was deposited on a glass surface via dip-coating. On the outermost polyanion layer a 0.37 g L⁻¹ aqueous solution of cationic poly(allylamine hydrochloride) with a M_w of 70 000 was printed.

3.3. Hot Melt Inkjet Printing of Waxes

Inkjet printing of (low-molecular-weight) waxes is somewhat outside the scope of the present contribution. However, the described results may have future impact on polymer inkjet printing. Hot melt inkjet-printed wax solidifies on contact with the substrate. This prevents spreading of the printed droplets, as permeation and evaporation do in the case of solvent-based inks. Changes in substrate and/or melt tempera-

ture can be used to create a variety of very fine patterns. Hot melt inkjet printing of waxes is a common technology in the graphical industry.^[48] Moreover, inkjet-printed wax masks for metal layer etching are beginning to appear in the field of electronics. Using a wax with a melting point of 80 °C, 20–40 μm diameter spots were printed with a drop placement accuracy better than 1 μm to fabricate masks for metal layer etching in a transistor.^[44,49] The performance of the transistor was equal to one made by lithography. Kemamide (13-*cis*-docosenoic amide) was used as wax.^[50] The spreading and stability of printed wax drops and lines, and three-dimensional wax structure printing, were studied from a fundamental viewpoint by Sonin and co-workers.^[51]

3.4. Three-Dimensional Printing of Ceramics

Three-dimensional printing is a technique for rapid prototype production, related in that sense to a number of other mold-free manufacturing techniques that aim to create a complex shape directly from a computer file. In ‘laminated object manufacture’ layers of laser-cut foil are stacked to produce the desired shape. In ‘selective laser sintering’ a deposit of powdered metal, polymer, or ceramic is scanned and sintered by a powerful laser. In stereo-lithography an ultraviolet laser scans an UV-curable resin. Finally, in three-dimensional printing a mechanically compacted layer of ceramic powder is imprinted using a binder solution as ink.^[52] This process is repeated slice after slice to create the object. Figure 7 shows a schematic picture of the three-dimensional printing process.

Moon et al. carried out an extensive investigation of various polymeric binder solution types,^[53] using a Hewlett Packard DeskJet 400 inkjet printer. Aqueous solutions of poly(acrylic acid) (PAA, M_w 5000) were tested, as well as poly[styrene-*co*-(acrylic acid)] (Joncryl, M_w 1700, 4900, 6500, 12 500), and an acrylic copolymer (Neocryl, M_w 20 000, 38 000). Solutions con-

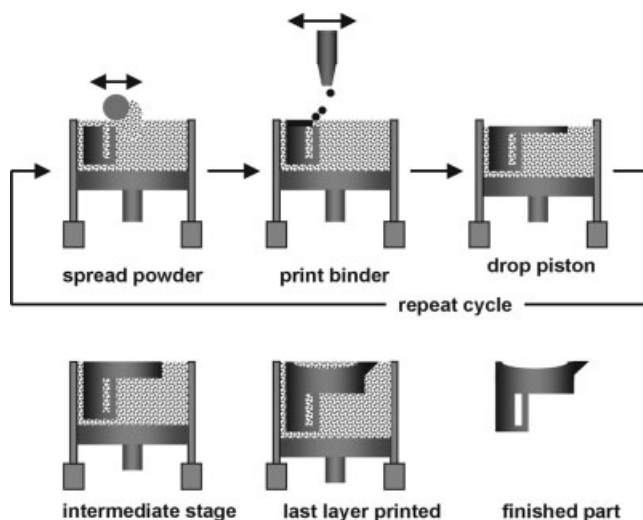


Figure 7. Schematic picture of the three-dimensional printing process.

tained 10 to 20 vol.-% of polymer. Viscosities measured at 300 s^{-1} varied between 2.9 and 9.0 mPa s, and surface tensions between 26.2 and 50.2 mN m^{-1} . The authors concluded that a molecular weight of 15 000 is an upper boundary for the use of a polymer as a binder due to poor penetration into the porous bed when using polymers with a higher molecular weight. Others have studied spreading, infiltration and surface adsorption of inkjet-printed polymer solution droplets on porous powder beds consisting of high-purity alumina.^[54] An aqueous solution of poly(acrylic acid) (PAA, M_w 60 000) was used, containing 2.4 vol.-% PAA.

A rather unusual way to bind ceramic particles was proposed by Calvert et al.^[55] It was found that an insoluble gel was formed by alternating inkjet printed layers of cationic and anionic polyelectrolytes, which were annealed overnight in a humid environment at 50 °C. The gel could fix a porous layer of alumina particles. Poly(dimethyldiallylammonium chloride) was used as the cationic polyelectrolyte, designated 'very low M_w '. The anionic polyelectrolyte was poly[(styrene sulfonate)-*co*-maleate] 3:1, M_w 20 000. A piezoelectric Microfab print head was utilized in combination with an Asymtek fluid dispenser platform.

In contrast to layer-wise imprinting of ceramic powder with a polymeric binder, an object can in principle be printed directly using ink containing dispersed ceramic particles plus polymeric binder. Blazdell and co-workers utilized ceramic ink containing zirconium^[56] and titanium dioxide.^[57] Poly(vinylbutyral) was used as binder (M_w 35 000–45 000). The authors showed that inkjet printing for ceramic manufacturing is achievable, but identified a number of problems, the most important being that only low volume fractions of ceramic particles could be printed (about 5 vol.-%). This in turn presented drying problems. A Biodot microdispenser was used as the printer. Even lower volume fraction suspensions of lead zirconium titanate (2.2 vol.-%) were printed, using polyvinyl acetate as binder.^[58] Bhatti et al. printed microscopic arrays of pillars from lead zirconium titanate (5 vol.-%) using an IBM Colorjet printer.^[59] To accelerate the drying process, printing was carried out at elevated temperatures, i.e., 50 °C. Poly(vinylbutyral) was used as the binder. An electron microscopy picture is shown in Figure 8. Using paraffin wax as the liquid carrier meant much higher volume fractions of solid material could be printed from the melt. Suspensions contained up to 40 vol.-% of α -alumina; this corresponded to the 40 mPa s viscosity threshold for printing, using the Modelmaker 6 Pro from Solidscape.^[60]

3.5. Life and Analytical Science Applications

Recently the use of inkjet printing was introduced for the preparation of monodisperse polymer microspheres for sustained drug release applications.^[61] The microspheres were made from biodegradable poly(lactic-*co*-glycolic acid) (PLGA) 85:15, and loaded with Paclitaxel, one of the best chemotherapeutic drugs developed in recent years. Micro-

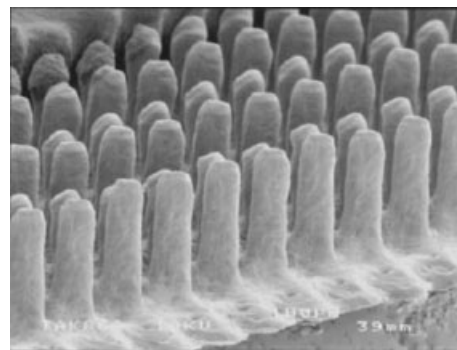


Figure 8. Electron microscopy picture of an array of pillars from lead zirconium titanate, inkjet printed by Bhatti et al. The pillars have an approximate height of 400 μm . (Reprinted from [59] with permission. Copyright 2001 Kluwer Academic Publishers).

spheres were fabricated by jetting a solution of PLGA and Paclitaxel in 1,2-dichloroethane into an aqueous surfactant solution. This solution contained 30 g L^{-1} PLGA. Evaporation and continuous stirring at room temperature removed the organic solvent. The Microfab Jetlab system was used as the printer.

Three-dimensional printing has been used for the manufacturing of drug delivery devices. A 5 wt.-% solution in chloroform of poly(ϵ -caprolactone), M_w 10 000–20 000 was printed on powdered poly(ethylene oxide) to create a dye-filled model drug delivery device.^[62] Multi-mechanism oral dosage forms were fabricated by inkjet printing of polymer solutions onto powdered mixtures of cellulose, lactose, and Eudragit L100 (poly[(methacrylic acid)-*co*-(methyl methacrylate)]), 1:1, M_w 135 000).^[63] Polymer solutions printed included a 20 wt.-% solution in ethanol of Eudragit E100 (poly[(butyl methacrylate)-*co*-(2-dimethylaminoethyl)methacrylate-*co*-(methyl methacrylate)]), 1:2:1, M_w 150 000), a 20 wt.-% solution in acetone of Eudragit RLPO (poly[(ethyl methacrylate)-*co*-(methyl methacrylate)-*co*-(trimethyl ammonioethyl methacrylate chloride)]), 5:10:1, M_w 150 000), a 5 wt.-% solution in water of Eudragit L100, and a 22 wt.-% solution in water of Kollidon K25 (poly(vinylpyrrolidone), M_w 28 000–34 000). Interestingly, a combinatorial approach was followed. A rectangular array of 9×10 dosage forms was printed simultaneously, using different binder solutions and varying amounts thereof.

Furthermore, inkjet printing is starting to play a role in the preparation of DNA microarrays.^[6] Oligonucleotide arrays were printed with both bubble-jet^[64] and piezo technology.^[65] Inkjet printing of an ink containing 1 g L^{-1} of a 600 base-pair DNA fragment was reported.^[66] GeSiM claims that inkjet printing of even larger fragments (2000 base-pairs, 1 g L^{-1}) is possible.^[16]

A recent development is the use of inkjet printing for the automated and reproducible preparation of sample arrays for matrix assisted laser desorption ionization time of flight mass spectroscopy (MALDI-TOF-MS).^[67] Both poly(ethylene glycol) (PEG, M_w 6000, 20 g L^{-1}) and poly(methyl methacrylate) (PMMA, M_w 14 400, 20 g L^{-1}) were printed using a Microdrop Autodrop system.

4. Physical Aspects of Polymer Inkjet Printing

Until now, few articles have been published that provide detailed information on how inkjet printability correlates with the rheological properties of a polymer-containing ink, and therefore with the polymer structure, molecular weight, and concentration. The work of Meyer et al. is a notable exception.^[68] The influence of added polymer on drop formation and filament break-up was studied at different concentrations, using various molecular weight polyacrylamides. Concentrations ranged from 0 to 200 ppm and molecular weights from 500 000 to 6×10^6 . Four different regimes were observed with increasing concentration or molecular weight. Normally, a long tail is formed that simultaneously disintegrates along its axis to form satellite droplets. At higher concentrations or molecular weights only a few satellites appear at the tails' ends. A single droplet without a tail represents the third regime. Finally, the droplet does not detach and returns into the nozzle. A scaling argument, taking into account only viscoelastic effects, showed that disintegration of the filament into small droplets does not occur if the typical Newtonian break-up time is smaller than the longest relaxation time of the polymer solution. However, as strain hardening was neglected the validity of this result is questionable. Recently a study using polystyrene solutions was published, also showing a decrease of printability with molecular weight.^[68]

Valuable information can also be found in studies on viscoelastic jet stability and the dynamics of drop formation. The relationships between (viscoelastic) jet stability and continuous inkjet printing, and between drop formation and DOD-inkjet printing, are obvious. In this section we will review some of the main results.

>An ordinary Newtonian jet is unstable to disturbances whose wavelength exceeds the diameter of the jet. This effect is known as the Rayleigh–Tomotika instability. The wave grows exponentially until the jet breaks to form droplets. The first experimental results on viscoelastic jet stability were published in the late 60s. The break-up length, i.e., the distance between the nozzle where the jet emerges and the point where the jet breaks up into droplets was studied using dilute solutions of polyisobutene in tetralin.^[69] A break-up length decrease with increasing elasticity or increasing molecular weight was found. Goldin et al. studied dilute aqueous solutions of highly branched carboxypolyethylene (Carbopol), poly(ethylene oxide), and poly(acryl amide) (Separan).^[70] It was found that the viscous but inelastic Carbopol solution behaved similarly to water. However, the viscoelastic solutions of Separan and poly(ethylene oxide) behaved totally differently. The growth of the wave was arrested, and strings of droplets connected by thinning filaments were formed. The filaments were remarkably persistent and the break-up length increased greatly. Figure 9 shows the effect of increasing molecular weight on fluid jet break-up and the formation of a bead-on-a-string structure. Later studies confirmed these findings.^[71,72]

Mun and co-workers investigated viscoelastic jet stability of poly(ethylene oxide) in glycerol/water, using molecular weights ranging from 8000 to 10^6 and differing concentra-

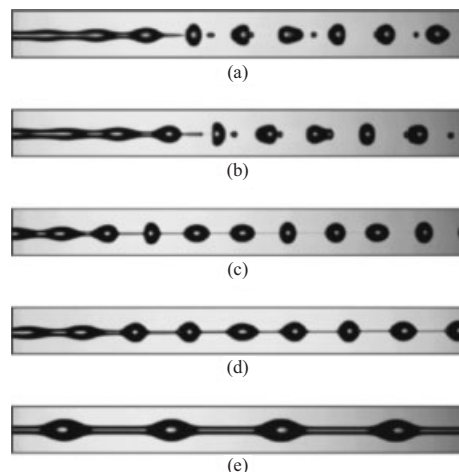


Figure 9. Series of pictures taken by Christanti and Walker, showing the influence of polymer molecular weight and concentration on the break-up of a fluid jet. Image size is 20 mm \times 2 mm. a) glycerol/water. b) 0.3 % 100 000 poly(ethylene oxide). c) 0.1 % 300 000 poly(ethylene oxide). d) 0.05 % 1 000 000 poly(ethylene oxide), e) 0.043 % 5 000 000 poly(ethylene oxide). The bead-on-a-string structure is formed when the molecular weight is equal or higher than 300 000. (Reprinted from [74c] with permission. Copyright 2002 Society of Rheology).

tions.^[73] Solvent composition was chosen such that all fluids had the same (shear) viscosity and surface tension. Above M_w 300 000 the break-up length increased and the bead-on-a-string structure was formed. Elongational viscosity measurements showed that above M_w 100 000 these fluids were strongly strain hardening, i.e., the elongational viscosity increased with elongation rate. Using the same fluids as Mun, Christanti and Walker showed that the elongation rate, $\dot{\epsilon}$, could be estimated from the thinning of the filaments connecting the beads, via $\dot{\epsilon} \approx -2/r(dr/dt)$, where r denotes the filament diameter.^[74] The measured elongation rates agree with the critical elongation rates discussed above where strain hardening was found, indicating that the elongational viscosity is the key rheological parameter governing jet break-up. In addition, it was shown that these filaments thin exponentially with time.^[74c] The measured relaxation time, τ , agrees qualitatively with the longest relaxation time according to the Zimm model, and scales with molecular weight as $\tau \propto M_w^{3\nu}$, as predicted by Zimm, where ν denotes the molecular expansion coefficient.^[75]

Studies on the dynamics of viscoelastic drop formation under gravity showed a behavior that in many respects resembles that of a viscoelastic jet. Experiments using fluids that were identical to those used by Mun revealed that in the case of a Newtonian drop a neck is formed that gradually thins prior to detachment, according to a power law.^[76] For viscoelastic fluids the neck eventually turns into a filament, sustained for a period of time that increases strongly with molecular weight. Pictures of the difference between Newtonian and viscoelastic drops are shown in Figure 10. Amarouchene et al. also found that the addition of small amounts of high

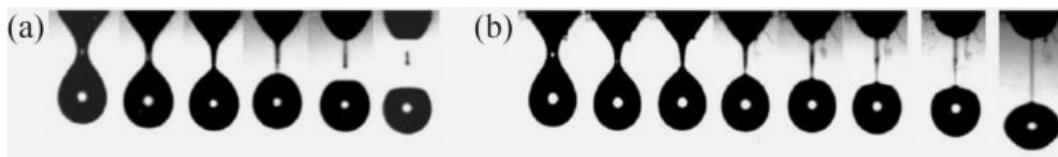


Figure 10. a) Formation of a Newtonian drop consisting of glycerol/water according to Cooper-White et al. Pictures are taken as a function of the time before detachment, in milliseconds. b) Effect of 0.1 wt.-% 1 000 000 poly(ethylene oxide). The drop is connected to the nozzle via a thinning filament. The time to break-up increases strongly. Droplet size is of the order of a few millimeters. (Reprinted from [76] with permission. Copyright 2002 Elsevier Science).

molecular weight poly(ethylene oxide) gave rise to long-lived cylindrical filaments.^[77] Filament thickness decreased exponentially with time. The fluids used were shown to be strain hardening. When using the rigid rod polymer xanthan (M_w of 3×10^6) the authors observed that thread formation and strain hardening were absent. Neck thickness followed the same power law as for Newtonian fluids.

5. Conclusions and Outlook

In this review we provide an overview of the state of the art in the field of polymer inkjet printing. Inkjet printing exists in a number of different forms. For polymer printing piezoelectrically driven drop-on-demand (DOD) inkjet printing seems the method of choice. Several applications of polymer inkjet printing were discussed. Within a few years inkjet printing has evolved from a technique to print individual polymer dots to the point where industrial manufacturing of multicolor polymer light-emitting diode (PLED) displays has become feasible. A polyacrylamide with a molecular weight of 6×10^6 seems to be the highest molecular weight polymer printed to date, although the printing of a poly(vinyl carbazol) with a molecular weight of 1.1×10^6 also represents an important example. In the related field of organic electronics, inkjet printing was used to fabricate thin film transistors and circuits based thereon. A frequently used polymer is Baytron-P, consisting of a high-molecular-weight poly(styrene sulfonic acid) backbone with conducting oligomeric poly(3,4-ethylenedioxythiophene) counter-ions. Molten waxes can be inkjet printed to fabricate cost-reducing etching masks, as compared to standard lithography. Inkjet printing has been applied to three-dimensional printing of ceramics, where some ceramic shape is formed layer by layer by printing a polymeric binder solution on compacted ceramic particles. The use of poly(acrylic acid) with a M_w of 60 000 was reported. Concentrations are typically of the order of a few percent by volume. However, it was shown that best results are obtained by using polymers whose molecular weight does not exceed $15\,000 \text{ g mol}^{-1}$, due to better penetration characteristics. Alternatively, dilute ceramic ink containing both ceramic particles and polymeric binders can be printed. The possibility of printing complicated shapes like microarrays of ceramic pillars was demonstrated, but attempts to use higher concentrations of both particles and

binder were unsuccessful. Oral dosage forms for controlled drug release were fabricated with three-dimensional inkjet printing, using highly concentrated (20 wt.-%) solutions of several Eudragit acrylic copolymers (M_w 135 000–150 000). Moreover, a new field where inkjet printing has been applied to is that of DNA microarrays.

Studies on viscoelastic jet stability revealed a strong influence of even small amounts of polymer. Solutions of sufficiently high molecular weight poly(ethylene oxide) and poly(acryl amide) showed a ‘bead-on-a-string’ structure, i.e., strings of droplets connected by thinning threads. The appearance of this structure is attributed to strain hardening, i.e., an increase of the elongational viscosity with elongation rate. Experiments on drop formation dynamics showed that polymer addition changes the drop development to break-off. A thin fluid thread is formed that is sustained for an amount of time that increases greatly with molecular weight. Thread thickness decreases exponentially with time. Interestingly, this behavior seems restricted to flexible polymers, whereas solutions of rod-like polymers behave like ordinary viscous fluids. For the future development of polymer inkjet printing, systematic study of inkjet printability of polymers in solution and polymer melts as a function of polymer structure, molecular weight, concentration, and solvent characteristics is a prerequisite. After exploring the inherent possibilities and limitations of the technique, strategies can be envisioned for printing a large number of different compounds in future. This would also open new avenues for the application of inkjet printing to combinatorial material research.

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