



Photopolymerisation in Spinning Disc Reactor

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Overview of presentation

- ❑ **Photopolymerisation chemistry**
- ❑ **SDR desirable characteristics**
- ❑ **Experimental data for photopolymerisation of n-butyl acrylate in SDR**
- ❑ **Conclusions**



Polymerisation types

2 types of polymerisation mechanism

Chain polymerisation

Free-radical

- Thermal initiation of an initiator
- Direct thermal initiation of a monomer
- Photo-initiation of an initiator

Cationic/
Anionic

Step-growth
polymerisation

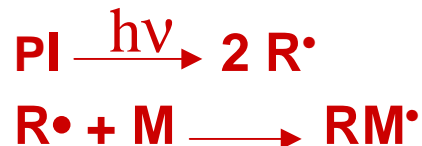
Reaction between
bi- or polyfunctional
monomers e.g
polyesterification



Photopolymerisation chemistry

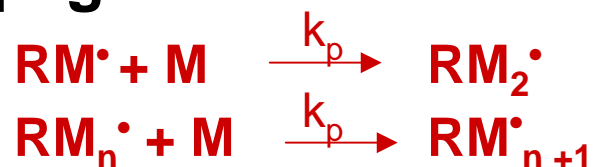
■ Free-radical mechanism:

□ Initiation



$$R_i = 2\Phi_i I_0 [1 - \exp(-\epsilon I [\text{PI}])]$$

□ Propagation



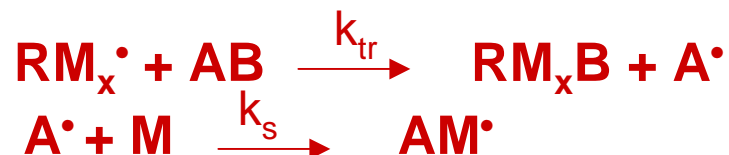
$$R_p = k_p [\text{M}][\text{M}^\bullet]$$

□ Termination



$$R_t = 2 k_t [\text{M}^\bullet]^2$$

□ Chain transfer



$$R_{tr} = k_{tr} [\text{M}^\bullet][\text{AB}]$$



Photopolymerisation chemistry

■ Quasi Steady State Assumption: $R_i = R_t$

□ Steady-state rate of polymerisation R_p :

$$R_p = -\frac{d[M]}{dt} = k_p[M] \sqrt{\frac{\Phi I_o \epsilon l [PI]}{k_t}}$$

$$X = 1 - \exp \left\{ \frac{-2 K_p}{\sqrt{K_t \phi \epsilon l}} \sqrt{\frac{[PI]_0}{I_o}} \left[1 - \exp \left(\frac{-1}{2 I_o \phi \epsilon l t} \right) \right] \right\}$$

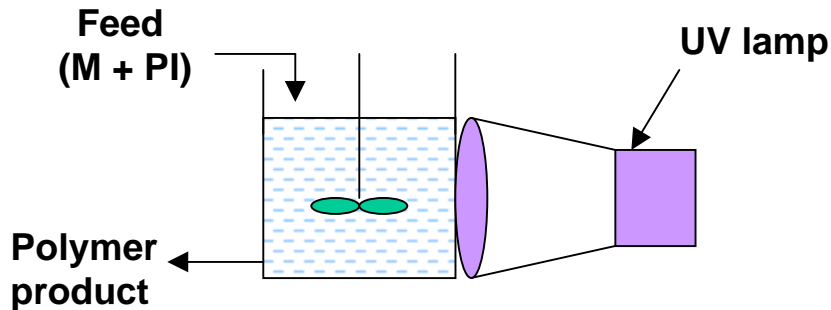
□ Steady-state kinetic chain length KCL:

$$KCL = \frac{k_p [M]}{2 \sqrt{k_t I_o \Phi l \epsilon [PI]}}$$



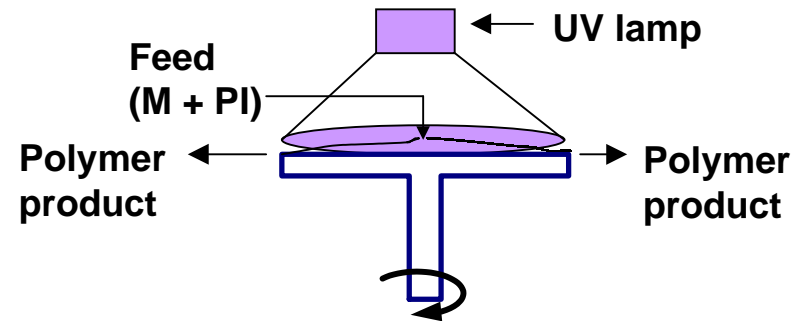
Why SDR for Photopolymerisation?

Conventional STR



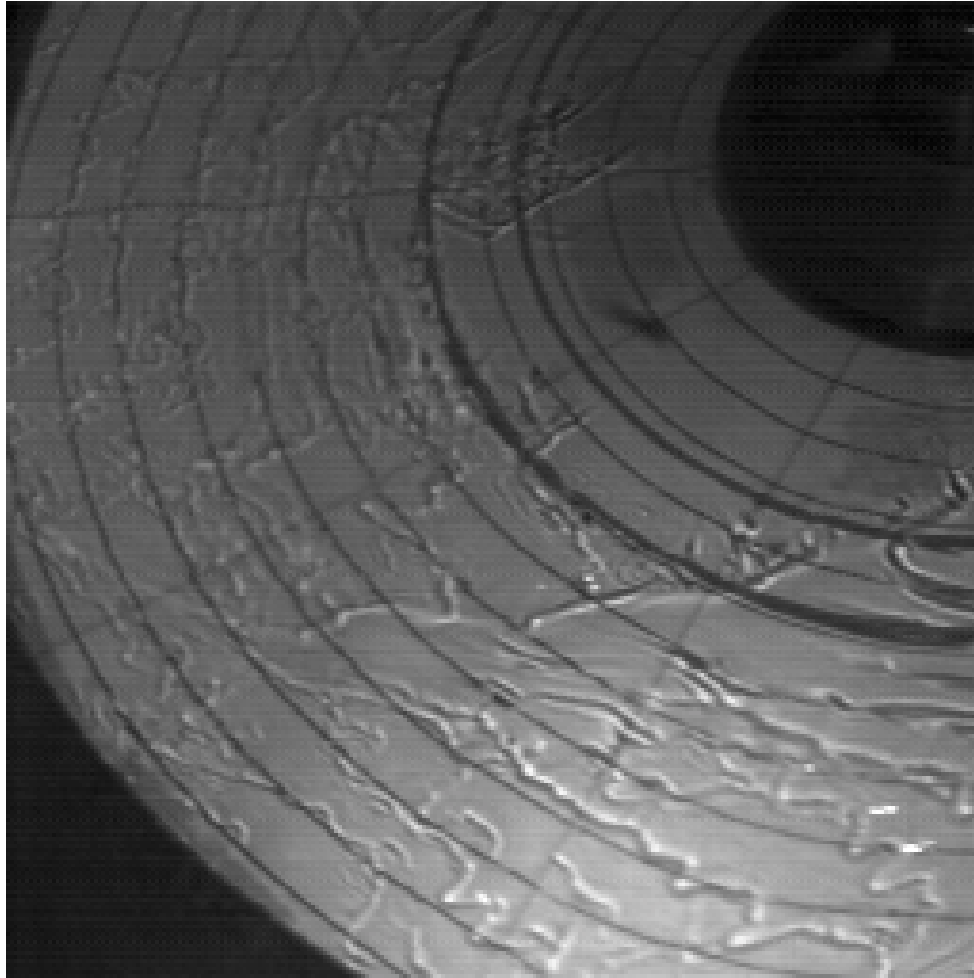
- Incident UV beam can only penetrate to a few mm into the bulk mixture
- Poor mixing in highly viscous material (diffusion limitations)
- Poor heat transfer through viscous mixture (loss of temperature control!!!)
- Usually large residence times of the order of hours (loss of mol. wt control)
- Polymer build up on reactor walls further reduces heat transfer rates

SDR

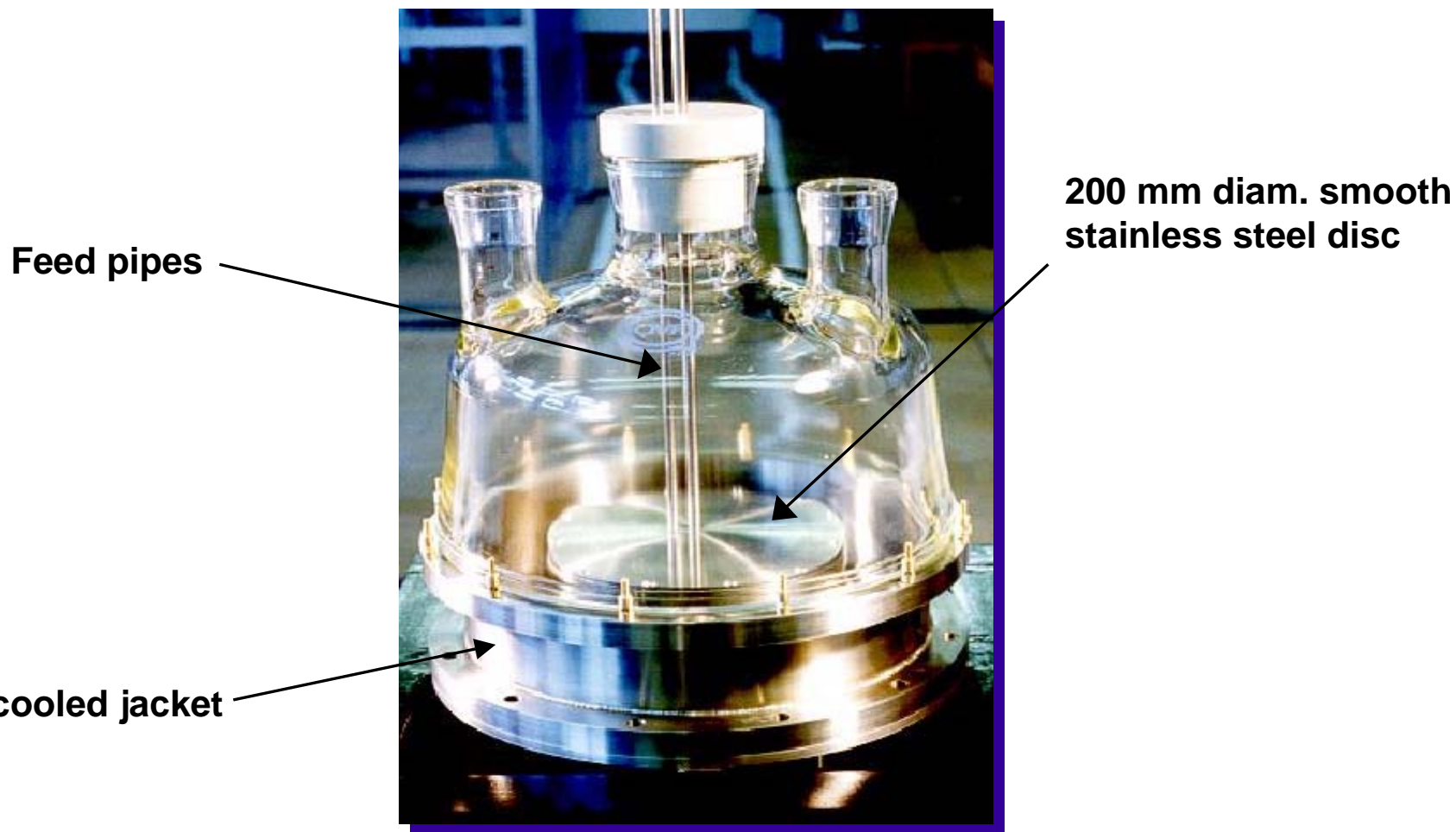


- ✓ Thin film (50-500 μm) for efficient UV penetration
- ✓ Intense mixing within film for intimate contact of various species (R^* , M , RMn^*)
- ✓ Rapid heat transfer for temperature control
- ✓ Short, controllable residence time for molecular weight control
- ✓ High centrifugal force gives minimal build up of polymer on reacting surface

Thin, Wavy Film Flow on Rotating Disc



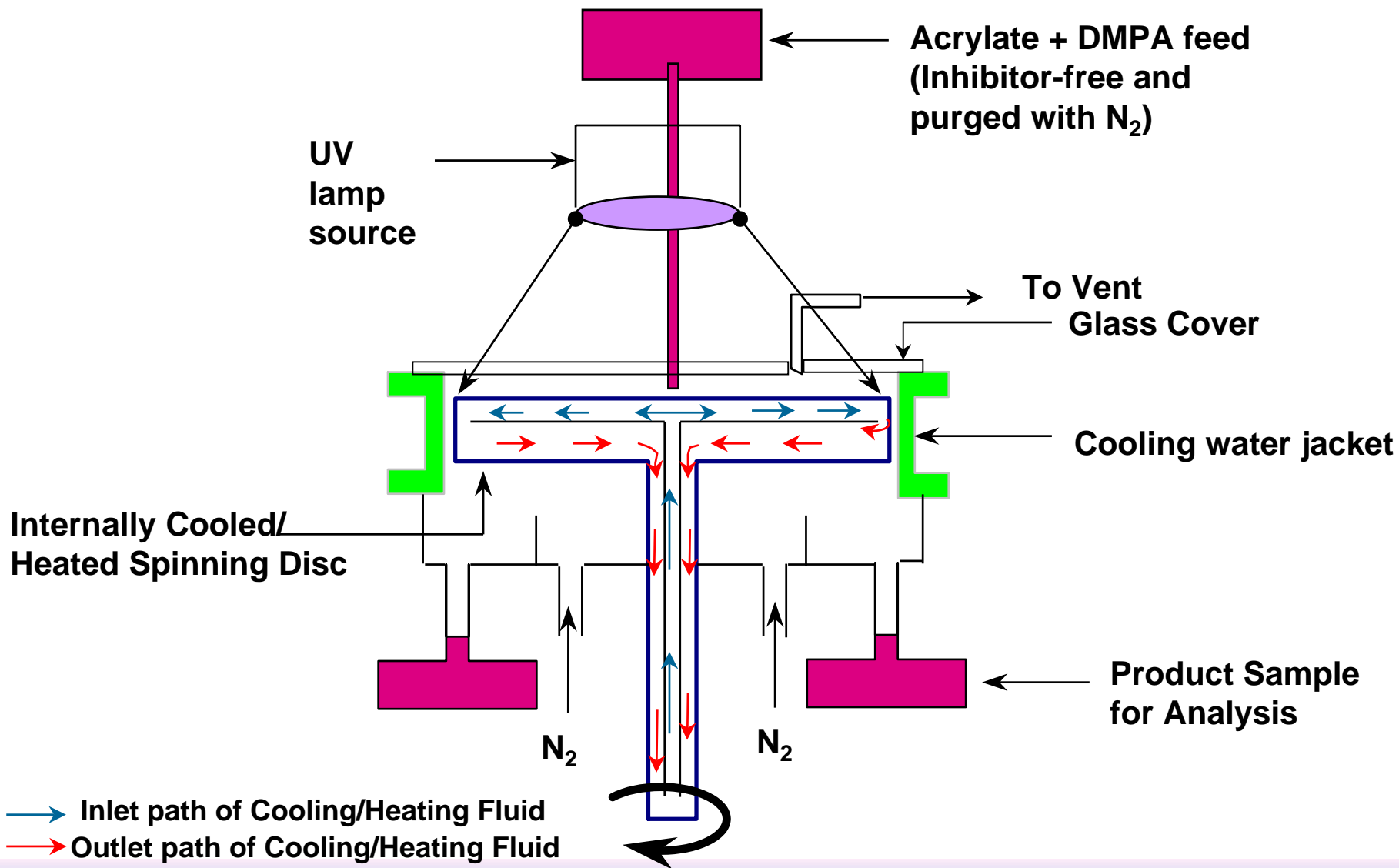
SDR set-up



Internally Cooled Spinning Disc Reactor



Schematic of SDR



Photopolymerisation of n-butyl acrylate in SDR

❑ Range of experimental variables tested:

- Disc rotational speed: 200-1000 rpm
- Monomer feed flowrates: 1 ml/s, 5 ml/s
- UV intensity: 25- 125 mW/cm²

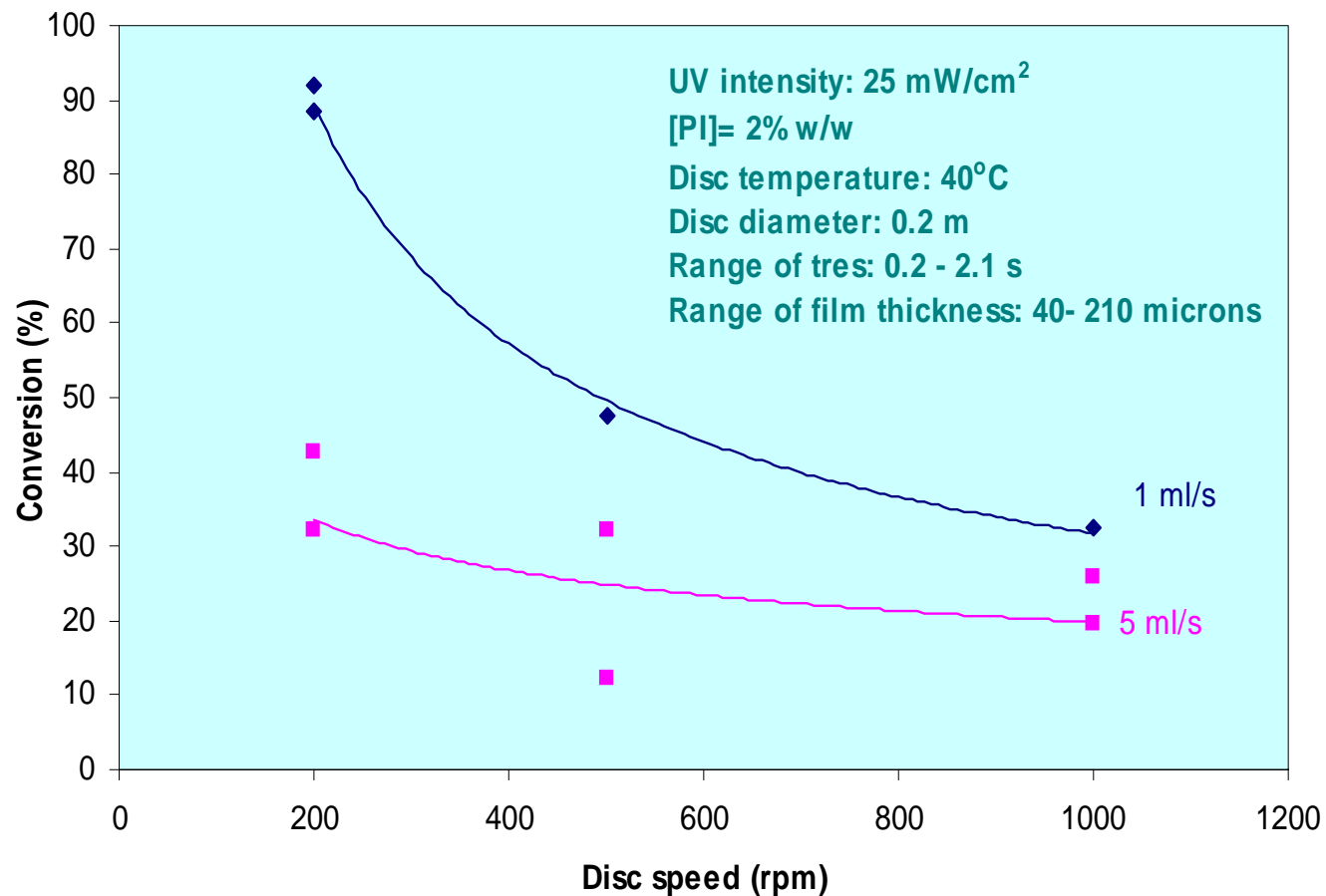
❑ Fixed variables: disc temperature (40°C), disc diameter (0.2 m), smooth disc, DMPA concentration (2% w/w), nitrogen flowrate (25 L/min)

❑ Measured variables:

- Conversion (GPC)
- Molecular weight properties (GPC)
(M_n, M_w, Polydispersity index)
- Branching effects (¹³C NMR)



Photopolymerisation of n-butyl acrylate in SDR



Influence of disc rotational speed and feed flowrate on conversion in SDR

Film thickness (δ) and residence time (t_{res}) in SDR

$$t_{res} = \left(\frac{81 \pi^2 \nu}{16 \omega^2 Q^2} \right)^{1/3} \left(r_o^{4/3} - r_i^{4/3} \right)$$

$$\delta = \left(\frac{3 \nu Q}{2 \pi \omega^2 r^2} \right)^{1/3}$$

Where

Q: feed flowrate

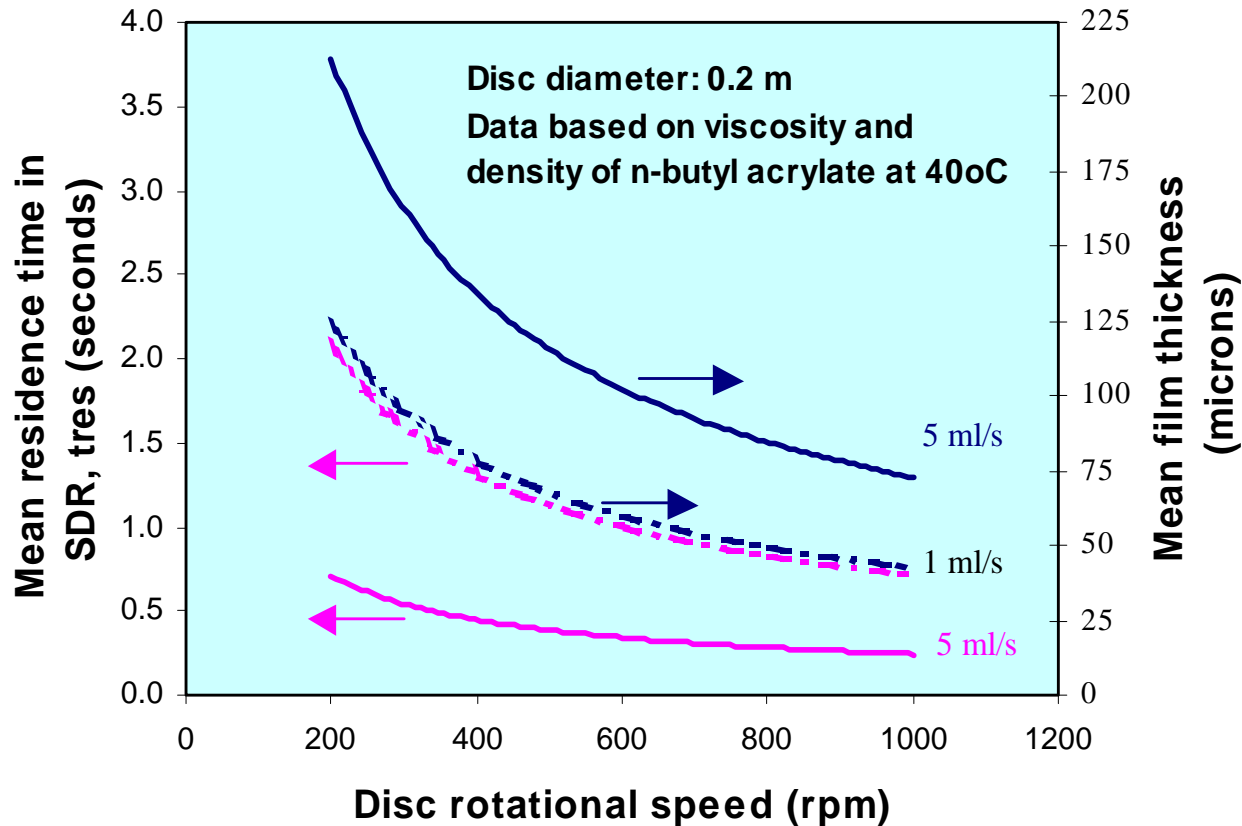
ν : kinematic viscosity ($=\eta/\rho$)

ω : rotational speed ($= 2\pi N/60$, N: speed in rpm)

r: radial distance across disc surface



Film thickness (δ) and residence time (t_{res}) in SDR



Mean residence time and film thickness profiles in SDR at different rotational speeds and feed flowrates



Film thickness (δ) and residence time (t_{res}): their influence on conversion in SDR

At feed flowrate of 1 ml/s and UV intensity of 25 mW/cm²:

Disc speed (rpm)	Mean δ (microns)	Mean t_{res} (s)	Conversion (%)
200	125	2.1	~90
1000	43	0.7	~32

Theoretically for photopolymerisation,

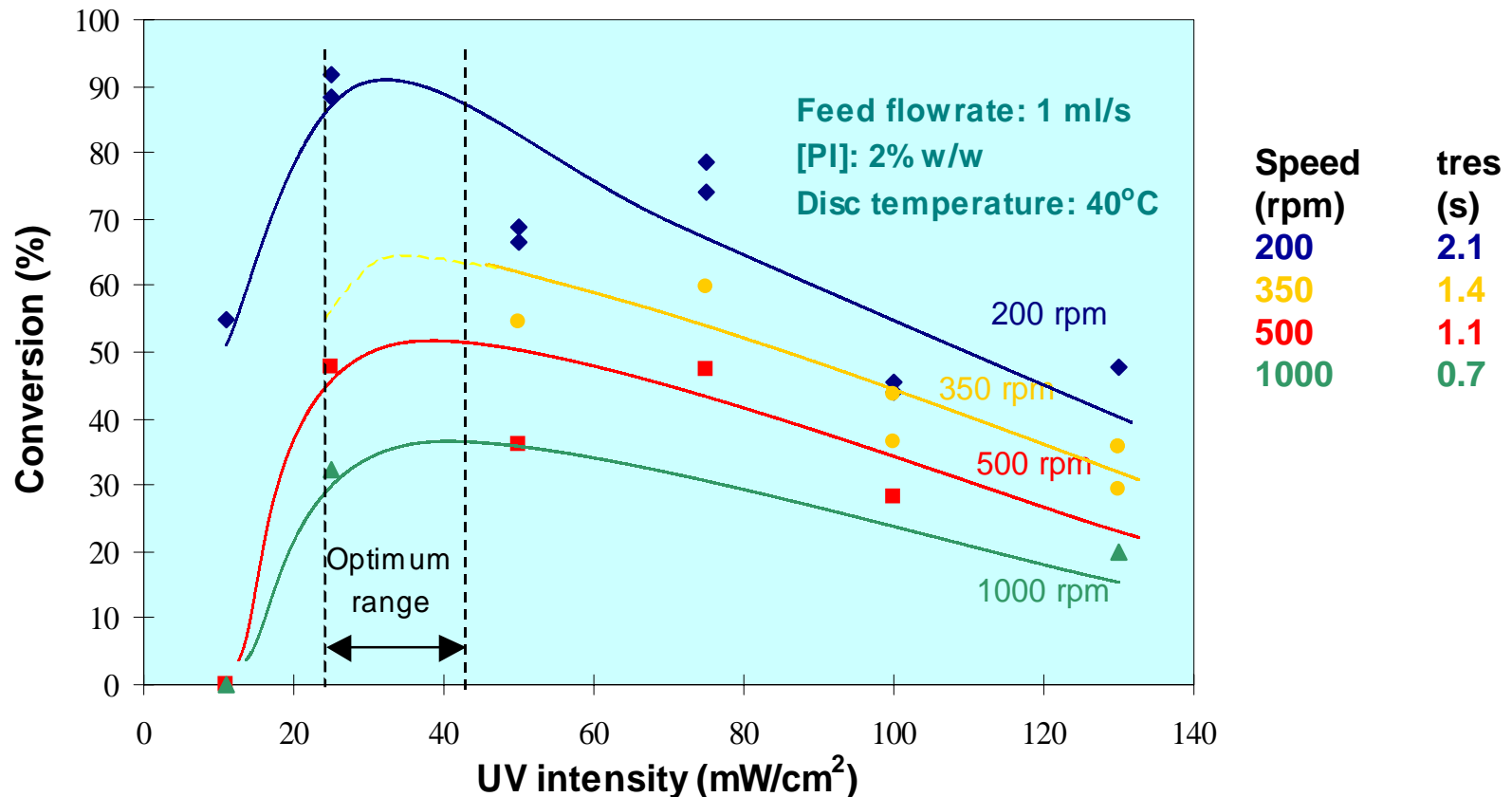
- Conversion increases with thinner films
- Conversion increases with higher UV exposure time

In SDR, t_{res} (or UV exposure time) appears to be the **more dominant** variable

⇒ **Higher conversion at lower disc rotational speeds which give larger residence times on the rotating disc**



Photopolymerisation of n-butyl acrylate in SDR

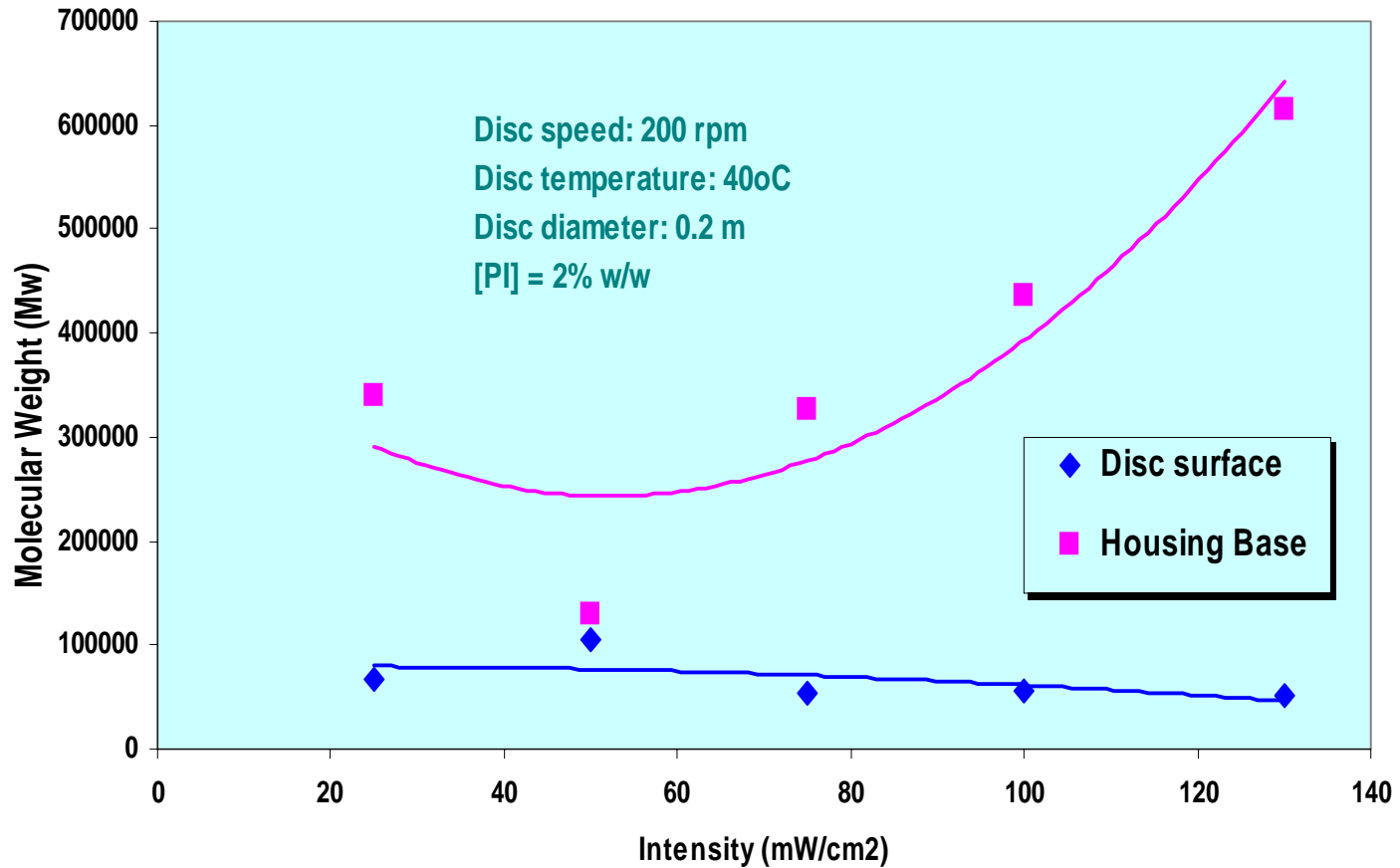


Influence of UV intensity on conversion in SDR

➔ Optimum UV intensity in 25-45 mW/cm² range for disc speeds tested

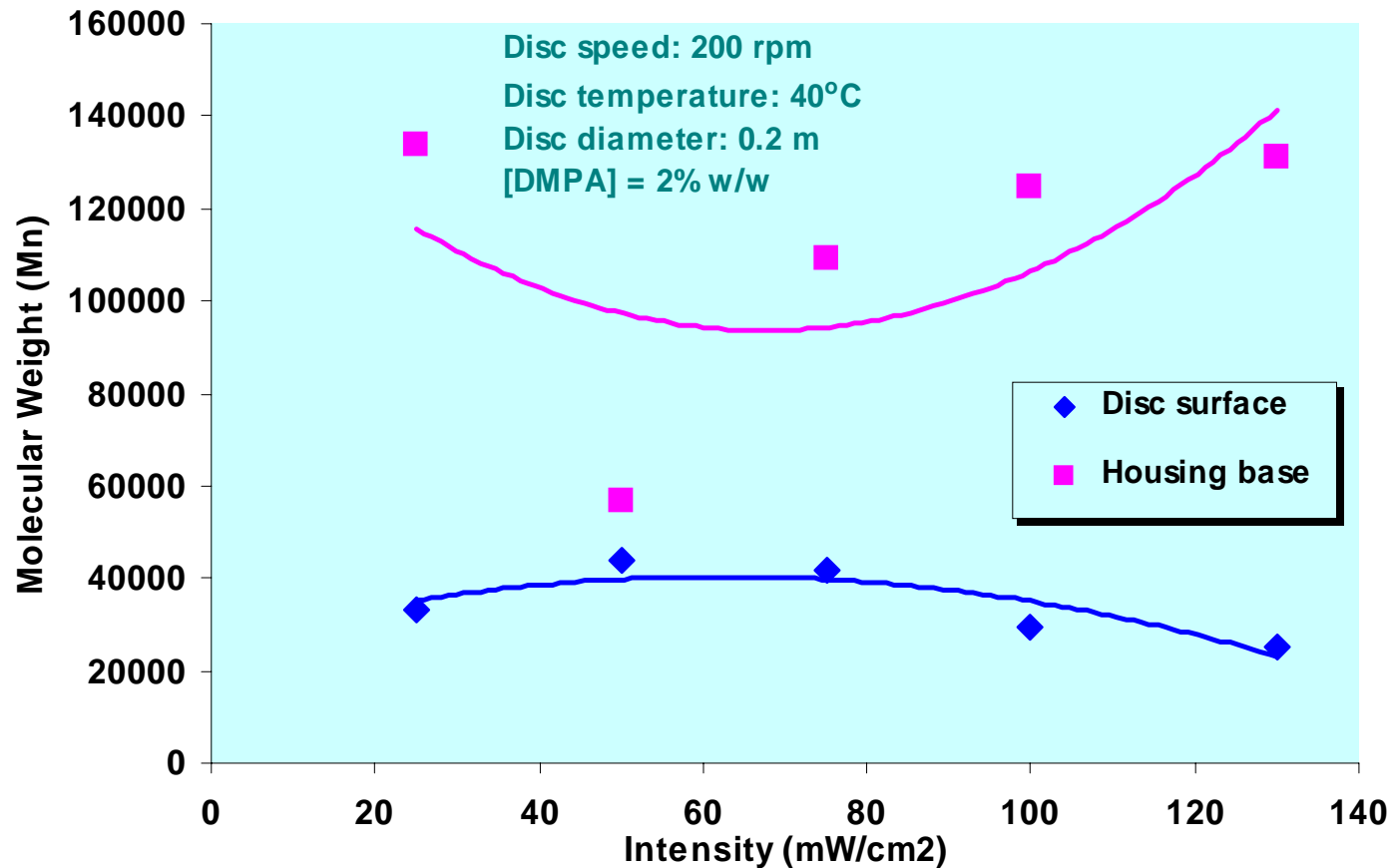


Molecular weight properties



Influence of UV intensity on Mw of polymer formed in SDR

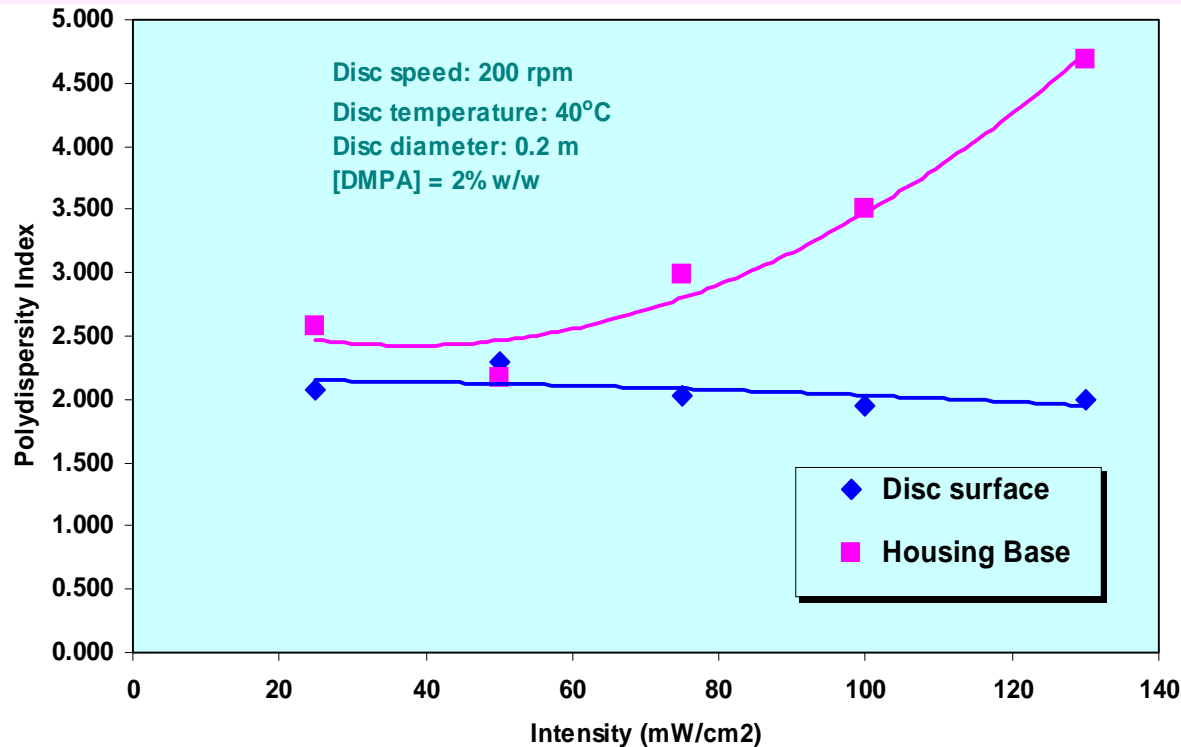
Molecular weight properties



Influence of UV intensity on Mn of polymer formed in SDR



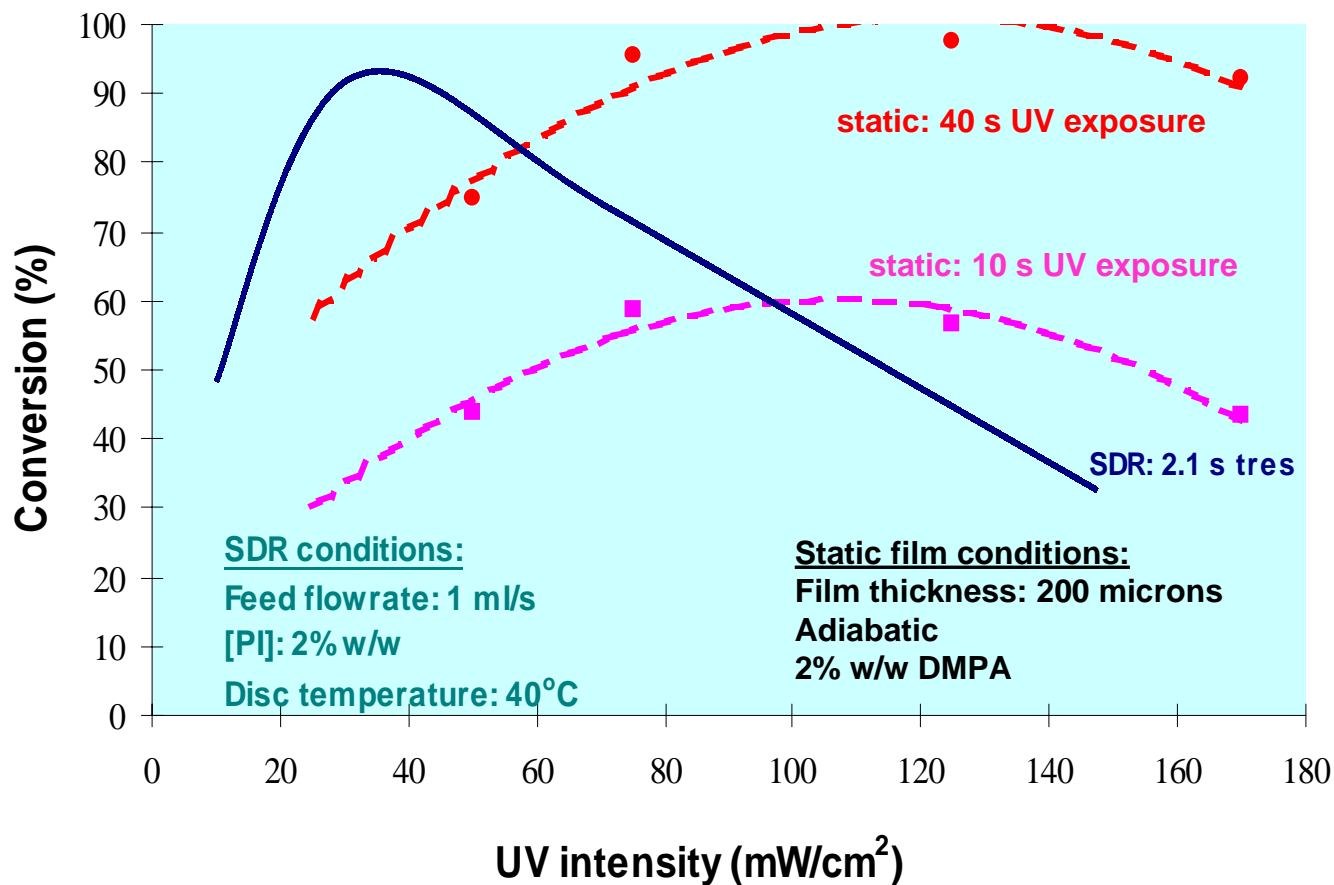
Molecular weight properties



Influence of UV intensity on polydispersity index of polymer formed in SDR

- Another interesting observation was that the SDR polymer formed was **linear even at very high conversion**, indicating the **suppression of chain transfer reaction** which under conventional reaction conditions is known to give rise to extensive branching in the polymerisation of acrylates

Static film vs. Thin, highly sheared film in SDR



Influence of UV intensity on conversion of n-BA in static films and in SDR thin films

Static film vs. Thin, highly sheared film in SDR

At 25 mW/cm² UV intensity:

□ Static film (200 microns)

- 30% conversion (10s exposure time)
- Mw~ 52,000
- Mn~ 28,000
- PDI~ 1.8

At 75 mW/cm²

- 92% conversion (40s exposure time)
- Mw~ 35,000
- Mn~ 18,000
- PDI~ 2.0

□ SDR thin film (~125 microns)

- 90% conversion (2.1 s exposure time)
- Mw ~70,000
- Mn ~33,000
- PDI ~2.1

SDR gives *higher conversion*, *higher molecular weights* with *good control of MWD* at *reduced exposure times* and *moderate UV intensities*



Possible kinetic behaviour in SDR

- Improved initiator efficiency f especially at high conversions/viscosity ?
- Chain extension in centrifugal field which restricts termination and allows addition of more monomer to the active radical ends ?



Conclusions

□ Effect on conversion in SDR photopolymerisation of n-BA of:

- UV intensity
 - maximum conversion in 25-40 mW/cm² range for conditions studied
- Disc speed
 - lower disc speed gives higher conversion for a given flowrate
- Feed flowrate
 - lower feed flowrate gives higher conversion for any given disc speed

► **Highest conversion of ~90% at 25mW/cm², 200 rpm and 1 ml/s**

□ Good control of molecular weight properties in SDR, also no branching

□ SDR outperforms photopolymerisation in thin static films

- Mixing plays an important role



Benefits of using SDR

- **Continuous reactor system producing thin, sustainable films**
- **Efficient utilisation of UV radiation**
- **Reduced processing time/lower energy consumption**
- **Improved product quality (linear polymer)**
- **Improved intrinsic safety (low hold-up volumes)**
- **Cleaner/greener process (no solvent)**
- **Distributed manufacturing**



Acknowledgement

- **Drs Bill Dunk and Roshan Jachuck for stimulating discussions**

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